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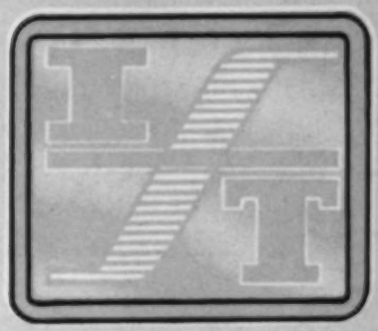

Volume IV, Number 4
April, 1950

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# Fifth Session of the FAO Conference

How well fed, clothed, and sheltered are the people of the world today?

How can the nations, through individual and joint action, improve the world food and agricultural situation?

These were the two main questions that the FAO Conference asked at its Fifth Session, held in Washington, D. C., November 21 to December 6. All Conference activity referred directly or indirectly to these questions.

The Conference answer to the first question states the world problem of food and agriculture today. The Conference answer to the second question constitutes a plan and a program for FAO and suggestions and recommendations to member governments on food and agriculture policy.

According to the picture presented to the Conference, total world agricultural production has regained prewar levels. But supplies available per person are below prewar, since population increased about 10 percent in the war and postwar period. For the world as a whole the supply per person would probably reach prewar levels in some six or seven years. In the Far East and Latin America it would take longer.

Some of the best-fed nations of the prewar period have become better fed; some of the worst, worse fed. Before the war about one-fifth of the population of the world had a daily diet of 2,000 calories or less. The number now on this inadequate diet has increased to about one-third of the world's population.

At the other end of the scale, three of the four countries outside Europe with a prewar daily diet of more than 3,000 calories have increased both calorie and protein intake.

About two-fifths of the world's food exports are from Canada and the United States, an increase in 10 years from less than one-seventh of the total. The United States share in world exports of bread grains rose from about one-tenth before the war to close to one-half since the war.

While the world is relying more heavily on dollar countries for both agricultural and industrial goods, the means of paying for them have decreased. Even present inadequate consumption levels of food-deficit countries are precariously held. Their gold and dollar reserves have been lowered. Loans and gifts on an unprecedented scale have been extended by Canada and the United States.

Any sudden fall in dollar earnings of the food-deficit countries or in volume of United States gifts and loans might bring about a food shortage in those countries and a surplus disposal problem in North America. Two requirements have to be met to effect a more balanced world agricultural economy. Efficient production in the soft-currency and underdeveloped areas must be expanded. And the high level of agricultural production and large volume of agricultural exports of North America must be maintained.

### Technical Assistance Program

The Conference declared that the expanded program of technical assistance, "more than any other program of international aid, can transform the lives of hundreds of millions of disadvantaged people." A resolution was passed accepting the program as previously approved by the Economic and Social Council and the General Assembly of the United Nations.

*President Truman Pledges Support.* In an address to the Conference President Truman emphasized the importance of the expanded technical assistance program. This, he said, was one of the great opportunities toward which he pointed in his inaugural address in January, 1949, when he spoke of the need for a bold new program for making the benefits of scientific advance and industrial progress available for the improvement of underdeveloped areas.

*International Investment.* The Conference stressed the need of increased international investment to make the expanded technical assistance program fully effective. Part of the assistance, it declared, should be used to help governments prepare over-all programs for agricultural development. It also suggested assistance for working out plans for specific individual development projects.

Governments were urged to prepare specific and well-documented projects and they were advised to call upon FAO for assistance in preparation of projects on a sound basis. The Director-General was instructed to report to the FAO Council and the Conference instances of suitable projects of significance which were unable to go forward for lack of adequate international financial facilities.

*Extension Services.* Great importance was placed by the Conference on effective extension and advisory services, especially in the technical assistance program. The greatest gap in knowledge within the field of FAO, it was asserted, is usually that between the producers, and not between the knowledge of experts in different countries. This gap can be bridged only by advisory and extension services.

The Conference specifically recommended that member countries strengthen their extension and advisory services. It asked the Director-General to provide advisory assistance in developing these services to governments requesting it.

### Distribution Problems

The Conference tackled the problem of how to maintain and expand high levels of agricultural production and consumption. "Unless a concerted effort is made to restore trade and payments equilibrium," stated the Conference report, "the persistence of present difficulties threatens to reverse the trend toward freedom from want. It would compel some of the largest surplus producing countries to restrict their agricultural production and deficit countries to expand at any cost."

Two lines of attack were suggested. The first comprised all measures which increase the dollar earnings of deficit countries, and the second encouraged a large and regular flow of investment from the hard to the soft currency area.

*ICCH Proposals.* Last June the Council of FAO authorized the Director-General to prepare a report on general and specific commodity problems, making use of the advice and assistance of experts in the field. The

report was completed and circulated to member countries in September. It recommended that the FAO Conference establish an International Commodity Clearing House (ICCH) whose function should be to move agricultural products from food-surplus, hard-currency areas into food-deficit, soft-currency areas.

The Conference debated the ICCH proposals at length and voted not to accept them. In respect to proposed short-term trading functions of ICCH, the Conference stated, "Any new international organization is undesirable unless it can be shown to be essential to carry out functions that cannot be performed equally well by an existing organization or by member governments directly involved."

It was suggested that provisions relating to financial difficulties in a particular commodity might be devised within the framework of individual commodity agreements. The principles governing international commodity agreements are set out in the ITO charter, which the Conference regretted has not yet come into force. However, some of the functions proposed for ITO have been delegated to the Interim Co-ordinating Committee for International Commodity Arrangements. The Conference recommended that FAO make greater use of ICCICA, since one of its three members is a representative of FAO.

The Conference recognized, however, that there is need for new machinery to deal with the surplus problem arising from balance of payments difficulties not covered by commodity agreements. To achieve this purpose it established an FAO Committee on Commodity Problems.

*New Committee at Work.* The FAO Committee on Commodity Problems is a subcommittee of the Council of FAO. It consists of representatvies of fourteen FAO member governments. At a meeting held following the close of the Conference session, the Council named the following governments members of the Committee: Australia, Brazil, Canada, Cuba, Egypt, France, India, Indonesia, Netherlands, Pakistan, Poland, United Kingdom, United States of America, and Uruguay.

The Committee held its first meeting in Washington on 12 and 13 January. It elected N. G. Abhyankar of India chairman and G. S. H. Barton of Canada vice-chairman.

The function of the committee is to help effect arrangements between governments for distributing surplus agricultural commodities to needy countries.

—*FAO Bulletin*, Jan.-Feb., 1950

# Student Chapters, I.F.T.

The National Council of the I. F. T. has authorized the establishment of Student Chapters at educational institutions where a minimum of ten Student Members are registered. Article XV of the National Constitution clearly states the requirements and procedure for the certification of such Student Chapters. For the benefit of interested and qualified universities and colleges Article XV is reprinted in its entirety:

## ARTICLE XV

### Student Chapters

"Section 1. The Council is empowered to grant authority, in the form of a certificate, to organizations of Student Members of the Institute attending any one educational institution for the establishment of Student Chapters. The authority will be granted when 1. an organization of Student Members petitions the Council for authority to designate itself a Student Chapter of the Institute, and 2. the Council has ascertained that the conditions prescribed in this Article for such authorization have been met, and 3. the petitioning organization of Student Members agrees to conduct its affairs in the manner provided for later in this Article.

"Section 2. Ten Student Members registered in any one educatfonal institution shall be the minimum permissible for recognition as a Student Chapter.

"Section 3. Authority for the establishment of a Student Chapter shall be withheld unless the petitioning oganization of Student Members shall have had a uninterrupted continuity of existence for a sufficient length of time to satisfy the Council as to the enduring character of the petitioners' purpose; provided, 1. that this period shall not be less than one year during which the petitioning organization shall have held at least three announced meetings per year; 2. that the officers of the petitioning oganization have been Student Members of the Institute in good standing for a minimum of one year; 3. that the petitioning organization is recognized as a campus group by the educational institution; 4. that the petitioning organization is sponsored by at least one member of the faculty who is also a member of the Institute. Further requirement is that the regional section of the Institute, within whose geographic boundaries the petitioning organization lies, advises the Council of its active sponsorship of the petitioning organization.

"Section 4. The Council may by affirmative vote terminate the Certificate of a Student Chapter when: 1. it ceases to function as a chapter for a period of more than one year; 2. it holds less than three announced meetings per year; 3. its membership is less than ten Student Members of the Institute; 4. it fails to maintain recognition as a campus organization; 5. it loses sponsorship by at least one member of the faculty who is a member of the Institute or 6. it loses the sponsorship of the regional section of the Institute in its geographical area.

"Section 5. Membership in Student Chapters shall be limited to Student Members. Assump-

tion is that Student Chapters will form the nuclei of Student Food Technology Clubs whose membership shall be open to all persons registered in their educational institutions indicating an interest in food technology.

"Section 6. Student Chapters shall have no representation in the Council of the Institute."

At present, there is no separate application blank for Student Members. The regular blanks may be used with the word "Student" inserted before "Membership" in the title. Blank forms may be obtained from Col. Charles S. Lawrence, Executive Secretary, I. F. T., Suite 954, 222 West Adams Street, Chicago 6, Illinois. He will also supply copies of the Constitution to interested members.

Essentially, at least ten Student Members must be active for at least a year prior to receiving a certificate from the Council as a Student Chapter. For a $2.50 membership fee the student receives a year's subscription to the journal FOOD TECHNOLOGY. This is much less than the actual cost of publication.

All educational institutions teaching food technology or closely allied fields in which there is an interest in food technology are urged to organize a group of Student Members and complete the requirements as set forth in Article XV. Several Student Chapters are now in process of organization.

STUDENT MEMBERSHIP COMMITTEE
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# Activity of Wetting Agents — Temperature Effects[a]

F. H. LUCAS AND A. H. BROWN
*Western Regional Research Laboratory,[b] Albany, California*

(Received for publication, July 27, 1949)

**The effect of temperature on wetting power was determined by the method of Draves and Clarkson for various surface active agents in both dilute sulfuric acid and water solutions over a temperature range of 25 to 95° C. Temperature effects were large for many of the types of wetting agents commonly used, and were increased by decreasing concentration of agent and by the presence of acid. The selection and use of wetting agents based on the experimental results reported are discussed in connection with certain processing operations.**

## Introduction

Need for a study of the effect of temperature on wetting-agent activity arose during experiments on the acid peeling of peaches. Peaches have been peeled with lye solutions for many years, but the fruit tends to discolor during and after peeling, particularly in the red pigmented portions. The discoloration is a serious disadvantage in the frozen food industry.

In contrast, acid peeling actually brightens both the red and yellow pigments of the peach. Hot-acid peeling of peaches, with and without the aid of wetting agents, has been previously reported by Olsen *(8)*, but the work was limited to temperatures below 60° C. as recommended by Woodroof *(9)*. Our studies were carried out at higher temperatures with the object of increasing peeling rates and minimizing heat penetration. Preliminary tests showed that 5% aqueous sulfuric acid solution peeled peaches in several seconds at 99° C., and in several minutes at 70° C. Uniformity of peeling was unsatisfactory because of variations in fruit ripeness and because of failure of the solution to wet the fruit.

To assist in wetting, a readily available surface-active agent was tried in the acid bath, but peeling was not improved. In view of favorable reports on the use of wetting agents in chemical peeling of fruits at lower temperatures *(8)*, further consideration was given to the proper selection of such agents for our work.

Many surface-active agents are available commercially and are classified broadly according to their ionization in aqueous solution. Those which do not ionize are classified as "non-ionic," whereas those which do ionize are classified as "cationic" or "anionic," depending upon the nature of the organic ion formed in solution. Most surface-active agents on the market, particularly those for domestic use, are of the anionic type. Many of these excel soap in wetting power; their use, toxicity, and antiseptic properties are similar to those of soap. The cationic agents are quite different from the anionic group in application and cost. Some of the quaternary ammonium cationic agents are outstanding germicides. The cationics are generally inferior to the anionics as detergents, but may show superior wetting ability. The cationic agents offer little competition to the anionic agents in wetting and cleaning operations because of a several-fold difference in cost. Non-ionic agents may show excellent wetting properties, but few are good detergents. Certain of the group find application as emulsifiers and for special functions in food products.

When the wetting agent first tried in our peach-peeling studies did not improve the operation, further information was sought concerning the proper selection and use of wetting agents in the application. A literature search revealed no pertinent information concerning the behavior of wetting agents at temperatures above 70° C.; few data were found to indicate the effect of acid solutions on the agents. Reported data indicated general improvement of wetting power as temperature increased in the range of 30° to 70° C. In consequence,

[a] Presented at the Ninth Annual Convention, I. F. T., San Francisco, Calif., July 12, 1949.

[b] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

laboratory wetting-time tests were undertaken to evaluate the usefulness of selected surface-active agents in 5% sulfuric acid solution over the temperature range of 25° to 95° C. For comparison, tests were also made on the agents in water over the same temperature range.

### Experimental Procedure and Results

Selected surface-active agents were first checked for stability in 5% sulfuric acid solution maintained at the boiling point of water for several hours. The twelve non-ionic agents tested were hydrolyzed by the hot acid. Alkyl sulfates, sulfonated amides, and esters which were tested were also hydrolyzed. Several cationic agents and the alkyl aryl sulfonate group of the anionic class were completely stable under the test conditions.

Agents which withstood the action of hot sulfuric acid were tested for wetting ability by the standard Draves and Clarkson wetting time test *(4, 5)*, employing a 3-gram hook exclusively. The test measures the time required for a weighted hank of standard cotton yarn to sink when immersed in a solution of wetting agent. The values of wetting time reported in this paper are averages of four individual tests. Consistent results could not be obtained at high temperatures without close control of the temperature of the test solution.

The results show that temperature has a pronounced effect on wetting time for most of the agents tested. General improvement is found as temperature increases from about 30° C. to a point in the range of 50° to 80° C. Further increase in temperature, up to about 85° to 90° C., seriously impairs the wetting power of many of the solutions tested. Near the boiling point of water, all agents appear to recover and to become excellent wetting agents. Thus, for many of the agents, the experimental curves of wetting time *vs.* temperature go through a minimum in the middle range of temperature, indicating optimum wetting temperatures for the particular agents under the test conditions; and through a maximum at a higher temperature, indicating zones of very poor wetting ability for the agents under the test conditions. Recovery of wetting power of aqueous solutions just below the boiling point has been observed before *(6)*, and seems to be a property of water rather than of the wetting agents. Curves O and P of Figure 4 show wetting times for water and for 5% sulfuric acid solution near their boiling points; the steepness of the curves demonstrates the necessity for close control of testing-solution temperature during wetting-time measurements at high temperatures.

The laboratory tests are summarized graphically as wetting time *vs.* temperature curves for various agents at one or more concentrations. Figure 1 includes curves for three anionic agents (alkyl aryl sulfonates) in acid solution; Figure 2 shows curves for two cationic agents in acid solution. The behavior in water of four anionic agents, including those of Figure 1, is shown in Figure 3. The curves for the cationic agents of Figure 2 in water are presented in Figure 4. Figures 5 and 6 include curves for two additional types of anionic agents and four non-ionic agents in water. The agents shown in Figures 5 and 6 were hydrolyzed by hot 5% sulfuric acid solution. Inspection of the curves shows that loss of wetting power at relatively high temperatures is most severe for the alkyl aryl sulfonates, and is accentuated by the presence of acid and by decreasing concentrations of the active agent.

A similar conclusion can not be drawn for the cationic agents. One performed better in acid solution; the other performed better in water. Intercomparison of the curves also shows a relation between the optimum wetting temperature and the inefficient wetting peak for the anionic agents, but not for the cationic agents. For the anionic agents, both points are shifted toward higher temperatures when the concentration of agent is increased, and toward lower temperatures when acid is added.

### Discussion of Results

The experimental results show why our peach-peeling operation was not improved by the addition of the wetting agent. General characteristics of the par-

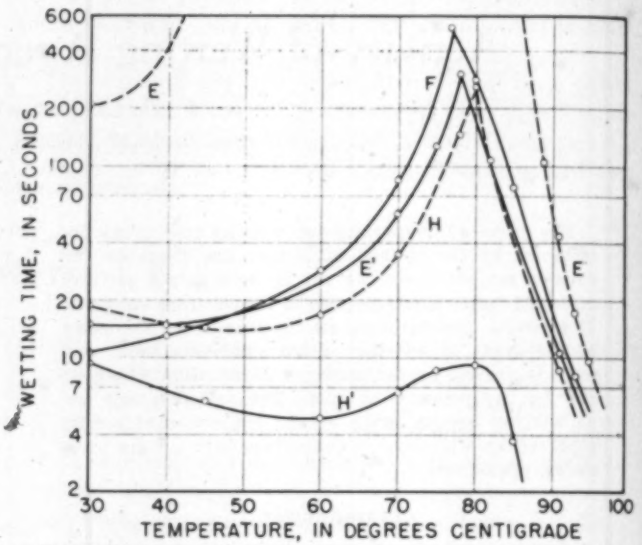


FIG. 1. Influence of temperature on wetting time of three alkyl aryl sulfonates in 5% sulfuric acid solution. Agent E, 0.10% by wt. Agent E', same as E except 0.25% by wt. Agent F, 0.25% by wt. Agent H, 0.10% by wt. Agent H', same as H except 0.25% by wt.

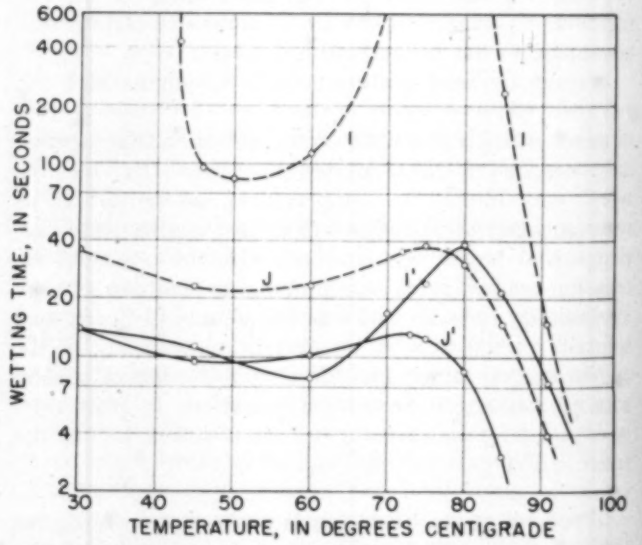


FIG. 2. Influence of temperature on wetting time of two cationic agents in 5% sulfuric acid solution. Agent I, 0.10% by wt. Agent I', same as I except 0.25% by wt. Agent J, 0.10% by wt. Agent J', same as J except 0.25% by wt.

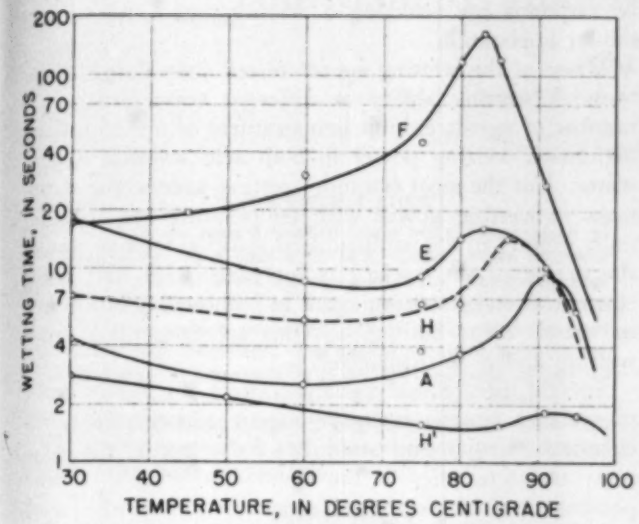


FIG. 3. Influence of temperature on wetting time of four anionic sulfonates in aqueous solution. Agent A, 0.05% by wt. Agent E, 0.25% by wt. Agent F, 0.25% by wt. Agent H, 0.10% by wt. Agent H', same as H except 0.25% by wt.

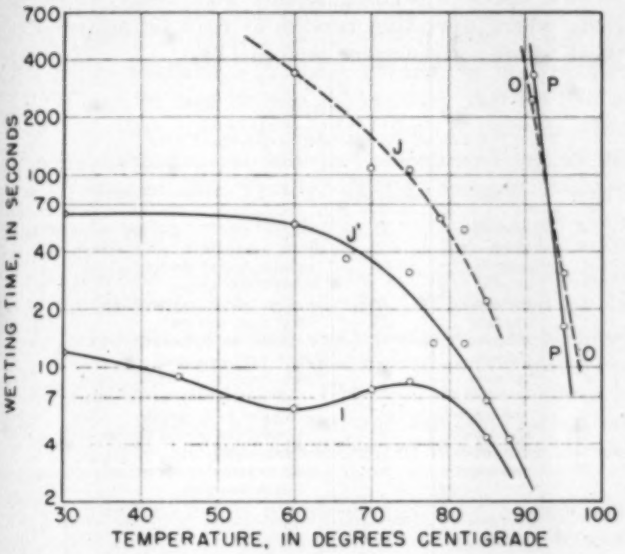


FIG. 4. Influence of temperature on wetting time of water, 5% sulfuric acid, and of two cationic agents in aqueous solution. Curve O, distilled water. Curve P, 5% sulfuric acid solution. Agent I, 0.25% by wt. Agent J, 0.10% by wt. Agent J', same as J. except 0.25% by wt.

ticular agent are shown in curves E and E', Figure 1; operating conditions were less favorable than indicated by the curves because the agent was used at an even lower concentration in the acid peeling bath. At the lower peeling temperature, about 70° C., peeling conditions approximate the worst possible wetting conditions for the agent. At the higher peeling temperature, the agent has good wetting power, but the effect of temperature is so great that maintenance of the bath near good wetting conditions is practically impossible. When a load of cold fruit is dumped into the hot peeling bath, the solution temperature is substantially lower at the peach surface than in the body of the liquid, and conditions at the peach surface are shifted sharply toward poor wetting. As shown by curve E, Figure 1, the wetting time on cotton yarn for a 0.1% solution of the agent changes more than 60-fold between 85° and 95° C.

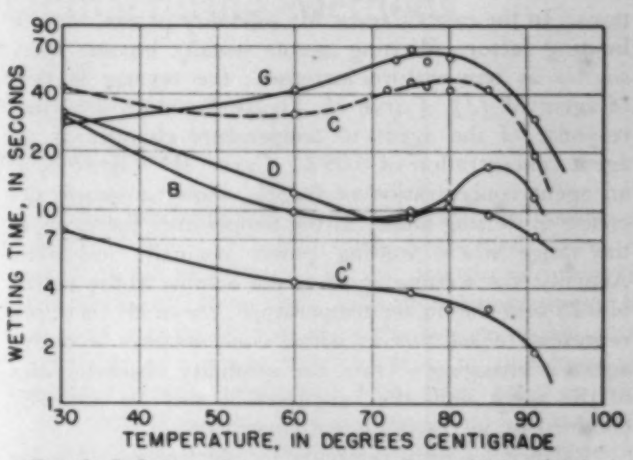


FIG. 5. Influence of temperature on four additional anionic agents in aqueous solution. Agent B, 0.25% by wt. Agent C, 0.05% by wt. Agent C', same as C except 0.25% by wt. Agent D, 0.25% by wt. Agent G, 0.25% by wt.

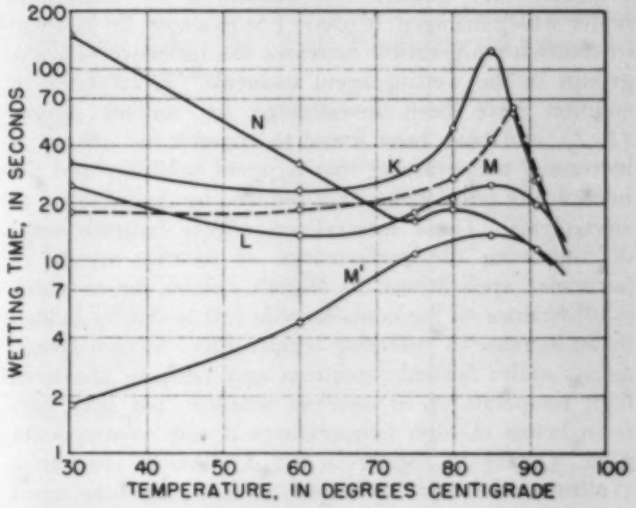


FIG. 6. Influence of temperature on wetting time of four nonionic agents in aqueous solution. Agent K, 0.05% by wt. Agent L, 0.25% by wt. Agent M, 0.05% by wt. Agent M', same as M except 0.25% by wt. Agent N, 0.25% by wt.

Wetting agent behavior is the result of a combination of factors, including the chemical identity and chemical stability of the agent, the concentration of agent used, solubility characteristics of the agent, and the "balance" or effective chemical relationship between the polar and non-polar parts of the molecule, particularly as affected by temperature and by electrolytes in solution. A short discussion of these factors may serve as a basis for explaining the reported results and as a guide in the selection and use of wetting agents for particular applications.

Our laboratory work involved the testing of a number of surface-active agents under fixed conditions. A wide range of wetting times was found, indicating that some of the materials tested were excellent wetting agents, others were poor wetting agents, under the test conditions. This result is expected in view of the variety of chemical compounds represented. For the same reason, many of the available agents were screened out before wetting-time tests were made, because of chemical instability in hot sulfuric acid solution. Different agents might have been selected for other test condi-

tions. In the case of agent M, solubility proved to be a limiting factor. Wetting agents usually become more soluble as temperature increases; the reverse is true of agent M *(3)*. Curve M, Figure 6, shows a normal response of the agent to temperature changes at an agent concentration of 0.05%. Curve M′, Figure 6, at an agent concentration of 0.25%, shows a steady decrease in wetting ability as the temperature increases in the range where wetting power normally improves. Actually, the wetting agent is not soluble to the extent of 0.25% at the higher temperature; curve M′ therefore represents a solution in which concentration of active agent is changing. Thus, the solubility characteristics of the agent limit the benefits that may be normally obtained by increasing agent concentration.

"Balance," a term referring to effectiveness of polar and nonpolar groups in a wetting agent, is a relative term. Designers of wetting agents may be forced to sacrifice balance to obtain adequate solubility; both solubility and balance are influenced by conditions under which the agent is used. For example, an increase in solution temperature increases the influence of polar groups in the wetting-agent molecule. Electrolytes in solution have been investigated for anionic agents *(1, 2)*, and have been found to counter the effects of increasing temperature; that is, agent solubility and the influence of polar groups are reduced by the presence of electrolytes. These interrelated effects indicate ways of improving the performance of wetting agents in particular applications. A slightly soluble agent which is off-balance on the nonpolar side will be doubly helped by an increase in operating temperature. Well-balanced agents under normal conditions may perform poorly at high temperatures in aqueous solution, but may perform better at high temperatures if salt solutions are used. Curves F, Figures 1 and 3, show an electrolyte (sulfuric acid) that is helpful to the particular agent below 60° C., and detrimental above 60° C.

As indicated by the foregoing data and discussion, wetting agents vary widely in their behavior under different conditions. For a particular application, consideration must be given to the type of agent, and to the conditions surrounding its use. If adjustments in temperature and electrolyte concentration are permissible, economies may be possible through the use of a cheaper agent adjusted to good wetting conditions in preference to a better, but more expensive, agent.

## Summary

To assist in the selection of a wetting agent for use in the experimental peeling of peaches in hot 5% sulfuric acid solution, relative wetting efficiencies of typical commercially important surface-active agents were determined by the method of Draves and Clarkson over the temperature range of 25° to 95° C., in acid solution and in water. Possible variations in the method are such that results may be of little value unless conditions of the test are rigidly defined and unless close control of solution temperature is maintained during high-temperature measurements. Further, there is no assurance that wetting-time tests on cotton yarn can be applied directly to actual wetting operations on other materials. Tests under actual operating conditions may be required for selecting a wetting agent for a particular application.

Many of the wetting agents tested show large variations in wetting ability at different temperatures. A number of agents exhibit temperatures of minimum and maximum wetting power in both acid solution and in water. For the most common wetting agents, the variations in wetting power with temperature are substantially greater in 5% sulfuric acid solution than in water; the extent of the variations increases with decreasing concentration of wetting agent in both acid solution and in water. Near boiling, aqueous solutions show good wetting ability in themselves.

Several interrelated variables affect the performance of wetting agents, including agent concentration, the chemical identity and stability of the agent, the solubility characteristics of the agent, and effects of temperature and of electrolyte concentration on the agent in solution. Intelligent selection and effective use of wetting agents depend upon an understanding of the influence of the variables. With a knowledge of these factors, users of wetting agents may reduce material costs where operating conditions may be adjusted to those where a given agent performs best.

TABLE 1

*List of Surface Active Agents Tested*

| Agent | Type | % Active Ingredient | Chemical Nature* |
|---|---|---|---|
| A | anionic | 85 | di-octyl ester of sodium sulfosuccinate |
| B | anionic | .... | fatty acid amide sulfonate |
| C | anionic | 90 | sodium lauryl sulfate |
| D | anionic | .... | substituted amide |
| E | anionic | 40 | sodium alkyl aryl sulfonate |
| F | anionic | 75 | alkyl aryl sulfonate |
| G | anionic | 25 | 7-ethyl-2-methyl-undecanol-4 |
| H | anionic | 85 | alkyl aryl sulfonate |
| I | cationic | 99 | high molecular weight amine |
| J | cationic | 100 | alkyl quaternary ammonium mixture |
| K | non-ionic | 87 | N-alkylol fatty amide |
| L | non-ionic | 99 | polyethylene glycol monolaurate |
| M | non-ionic | .... | ethoxy chain type |
| N | non-ionic | 97 | poly oxyethylene ether of sorbitan monolaurate |

* As described by manufacturer's publications or by McCutcheon *(7)*.

## Acknowledgment

Grateful acknowledgment is extended to E. J. Hoffman, who supervised the work reported and who conducted many of the tests.

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# Your Salt by Modern Manufacturing Methods

PAUL V. IMES
*The Carey Salt Company, Hutchinson, Kansas*

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**(REVIEW PAPER)**

**Ages ago man depended upon solar evaporation of sea water as a source of salt. Later, brine obtained from natural brine springs and wells was evaporated in small open kettles with fires underneath to speed the evaporative processes. These early methods were crude and inefficient. The grains obtained were coarse, irregular and impure, with hardly any resemblance to salt as we know it today. But, through years of scientific effort and applied engineering skill, most high quality evaporated salt is now made in economical vacuum flash evaporators.**

## Introduction

Salt—one of the most universally used, but least understood and little appreciated of all the necessities of life, without which man would perish—is one requisite which we take for granted *(1)*. Man's need for salt was experienced so early that no record of its actual discovery is available. Probably at first, in his primitive ignorance, he had no way of knowing that he had all the time been acquiring from the flesh of animals which he ate, minimum but sufficient amounts of salt for the sustenance of life. Finally, we may imagine, that he, quite by accident, tasted some of the impure, gleaming substance left encrusted along an ocean beach by the receding tide. Its distinctive taste impressed him when he placed some of it to his lips. When tried on his meat, its taste was much more pleasant. The salt had, as if by magic, revealed and enhanced certain tastes and flavors which he liked. His food tasted better, he seemed to possess more zest, and the substance which he had added to his food increased his feeling of well being *(3)*.

As a result of this means of discovery, ancient man depended upon solar evaporation of seawater, blocked off into small ponds, as a source of his salt. He did not know the secret of controlled selective crystallization used in modern times in the evaporation of natural brine, and consequently his salt was very impure, oftentimes a bitter, coarse and brown product that may have been mixed with sand or dirt. Contrast these impure, coarse particles—of necessity used by ancient man—to the dazzlingly white, pure, uniform crystals of today!

## Sources and General Nature of Natural Salt

Although early Americans were dependent entirely upon natural surface brine and brine springs, salt today is produced from underground mines, surface salt beds of dried up lakes, sea water, natural brine springs and man-made brine wells. There are approximately 70 plants operating in a dozen different states, and in recent years over 15 million tons of salt have been produced annually *(4)*. Present day commercial standards concerning quality and quantity have stimulated extensive developments for obtaining and processing salt from our vast underground deposits.

These underground Rock Salt deposits consist of stratified layers of salt in some areas, and domes or plugs of salt in others. The salt deposits occurring in the Michigan, New York, Ohio and Kansas areas, lie at quite varying depths below the surface of the earth, occurring as a single stratified layer or numerous associated layers interbedded with other salts or with some type of detritus rock such as shale. The rock salt is remarkably consistent in its thickness and continuous presence under these areas. Reserves of salt that occur in the known salt domes of Texas and Louisiana are also tremendous.

Of the vast tonnages of salt produced in the United States during 1946, 97% of the total was produced by only nine states *(8)*. Table 1 indicates the tonnages in all forms by states.

TABLE 1 *(4)*

*Production of Salt by States—1946*

| State | Percent of Total | Short Tons | Value |
|---|---|---|---|
| California | 5 | 729,092 | $ 3,358,060 |
| Kansas | 5 | 815,018 | 4,014,919 |
| Louisiana | 12 | 1,846,522 | 4,613,359 |
| Michigan | 29 | 4,334,202 | 15,711,074 |
| New Mexico (1) | | 8,677 | 16,399 |
| New York | 19 | 2,813,782 | 10,153,274 |
| Ohio | 17 | 2,645,995 | 4,160,011 |
| Puerto Rico (1) | | 12,411 | 83,494 |
| Texas | 7 | 1,098,589 | 1,356,676 |
| Utah | 1 | 121,669 | 339,505 |
| West Virginia | 2 | 272,841 | 896,894 |
| Other States (3) | 3 | 433,347 | 209,921 |
| Total | 100 | 15,132,145 | $44,912,586 |

(1) Less than 0.5 percent.
(3) Includes Nevada, Oklahoma and Virginia.

The producing salt beds agree very closely in purity of product, although some range as high as 99.8% Sodium Chloride, but the average for most mines in the United States is 98.3% *(2)*. Phalen *(7)* compares the composition of Rock Salt in New York and Kansas in Table 2:

TABLE 2 *(7)*

*Composition of Rock Salt*

| | New York | Kansas |
|---|---|---|
| | *Percent* | *Percent* |
| Chloride | 59.6 | 60.0 |
| Sodium | 38.9 | 38.6 |
| Sulfate | 1.2 | 0.8 |
| Magnesium | 0.1 | 0.1 |
| Calcium | 0.2 | 0.4 |
| Potassium | Trace | 0.1 |
| Carbonate | ..... | ..... |
| Bromide | ..... | ..... |
| | 100.0 | 100.0 |

## Recovery of Salt from Underground Rock Salt Beds

Rock Salt is recovered from subterranean levels by two systems. It is mined much like coal is mined and brought to the surface in solid form. The milling opera-

tions are usually performed on the surface where Rock Salt is crushed, processed, and graded by screening to the various sizes which are required for its many uses. The purities of rock salt are sufficient in many instances that it may be utilized for practically any use, including table salt.

Recovery of salt from the underground deposits may also be accomplished by a system known as Hydraulic Mining. In Hydraulic Mining, a well is drilled into the rock salt deposit, similar to an oil, gas or water well, and is fitted with two or more concentric pipes. Water is pumped down one pipe, preferably the inner one, at such a rate that it dissolves the salt while passing through a portion of the bed, becoming saturated, and is forced to the surface through the other pipe, by the incoming water. Air pressure is used as a booster in deeper wells. Artificially man-made brine, briefly described above, is saturated containing approximately 26 percent salt or 2.65 pounds to the gallon of brine. By comparison sea water contains about ¼ pound of salt to the gallon and Utah's Great Salt Lake about 2 pounds to the gallon.

### Processes of Evaporation to Recover Salt from Brine

Obviously, if salt in solid form is desired it must be recovered by evaporation, and the finished product is known as Evaporated Salt. The process of evaporation in a modern salt plant is much more complicated than merely permitting the water to evaporate and leave the salt behind. Solar evaporation is used principally on natural brine; artificial heat is used in grainer (open) pans and flash evaporators, both types of equipment being used by most manufacturers. Quantities of Evaporated Salt produced by States for the year 1946 are shown in Table 3:

TABLE 3 *(4)*

*Production of Evaporated Salt by States—1946*

| State | Percent of Total | Short Tons | Value |
|---|---|---|---|
| California | 18.3 | 595,747 | $ 2,988,775 |
| Kansas | 10.5 | 338,532 | 2,829,171 |
| Louisiana | 2.7 | 87,834 | 584,815 |
| Michigan | 29.4 | 953,183 | 8,162,183 |
| New York | 14.3 | 466,115 | 5,025,740 |
| Ohio | 14.0 | 456,227 | 3,615,003 |
| Puerto Rico | .4 | 12,411 | 83,494 |
| Utah | 3.5 | 115,248 | 310,610 |
| West Virginia | 4.2 | 136,320 | 883,393 |
| Other States | 2.7 | 87,840 | 503,271 |
| Total | 100.0 | 3,249,457 | $24,986,395 |

Purity of the finished product, by any method of evaporation, depends upon the degree of brine purification before evaporation into salt, and care in processing. The dissolved impurities that may occur in minute amounts in brine are principally calcium, magnesium, sulfates and bicarbonates, and they are readily removed by chemical treatment. Also, Calcium Sulfate is practically insoluble in brine that has been heated to a temperature of 300° F. (140° C.) so pre-heating of the brine is good practice. Sometimes a combination of chemical treatment and preheating is used, in which case the resulting salt purity is so near 100% that it is very difficult to detect any impurities at all. However, it is thought by some that salt of such high purity has lost its maximum saline effect. Traces of other salts, say two or three tenths of one percent may enhance the saltiness of Sodium Chloride. To my knowledge this thought has not been investigated by official taste panels, but if undertaken sometime I believe very interesting results would be found.

### Solar Evaporation

Solar evaporated salt is made from natural brine by selective fractional crystallization in large ponds which are harvested annually. The quality of modern day solar salt has benefitted too from the application of modern engineering methods and is a far step from that which was first made by man by the solar evaporation of natural brine. About 17 percent *(4)* of the evaporated salt produced in the United States is solar evaporated. It is sometimes purified further whereby some producers redissolve the initial salt obtained, purify the brine, then crystallize it by methods similar to those described below, using artificial heat.

### Grainer (Open) Pan Evaporation

The grainer (open) pan method is truly an American development. It is the oldest known commercial method used in the United States for the production of salt. Very few improvements have been developed over those methods used by the early salt producers. Most of the improvements have been of a mechanical nature such as the development of automatic rakes for removing the salt. The grainer pan method is very expensive and inefficient as compared to modern day flash evaporative techniques, and accounts for about 17 percent *(4)* of the total amount of evaporated salt produced.

The production of grainer salt started years ago incidental to some other industry. For instance, in Saginaw Valley, Michigan, the industry grew largely as an adjunct of lumbering because of the presence of cheap and readily available fuel in the form of waste from the saw mills; and the presence close by of natural brine. The disposal of this waste previous to the discovery of salt in the district had been costly. In this particular instance, the factors made possible a salt so inexpensive that the western market for New York Salt was completely destroyed. In the Ohio River Valley, coal mines and cheap power were early factors to the development of salt in this district, using grainer pans. We see, advantage was taken of the low cost of heat *(6)*.

Today Grainer Salt, commonly called Flake Salt is produced in huge, shallow tanks or pans often 150′ in length, 18′ wide and 2′ deep. The pan is usually provided with a hood as a protection from contamination and to vent to the outside of the building the vapors coming from the pan. Low pressure steam is passed through metal pipes immersed in the brine and this causes the water to evaporate. Brine flows in continually from supply tanks and salt which sinks to the bottom is mechanically raked to one end of the pan to be removed. The brine does not boil, and evaporation takes place on the quiet surface, without agitation. Temperatures may range from 140° F. (60° C.) to 200° F. (93.3° C.) and the type of crystal and especially size of

crystal is very much dependent upon temperature of evaporation. Dr. Looker mentions that all salt is basically a symmetrical cube *(5)*. Grainer processed salt crystals start as a tiny, pinpoint crystal cube, but as other cube-shaped crystals form they tend to cluster, slowly sinking a trifle in the brine as the cluster grows, so that with newer crystals clinging to the center crystal there is formed what may be described as hoppers or inverted hollow square pyramids. Many of the larger hopper-like crystals become broken in processing, thus the finished grade consists of tiny cubes or small numbers of cube cluster fragments.

You may logically ask the question, "Is grainer flake salt required, or just desired for some industrial processes?" Its continued use, I think, is traditional, and a carryover among certain users from the type of salt available to early Americans. True, most all manufacturers of evaporated salt produce grainer salt, but that is necessary only so long as certain customers desire it for their operations. I believe most modern food processors, in continually improving the efficiency and economy of their own operations in these modern, competitive days, may logically look to the use of economical, clean, pure, uniformly screened Flash Evaporated Salt.

### Vacuum Flash Evaporators

What are the latest developments and principles involved in the evaporation of brine to make high quality salt by flash evaporators, or more especially by economical *vacuum* flash evaporators? The greatest improvement is to place the brine under conditions of reduced pressure, thereby lowering the boiling point. This is best brought about by use of batteries of closed kettles (Note Figure 1) and by proper regulation of

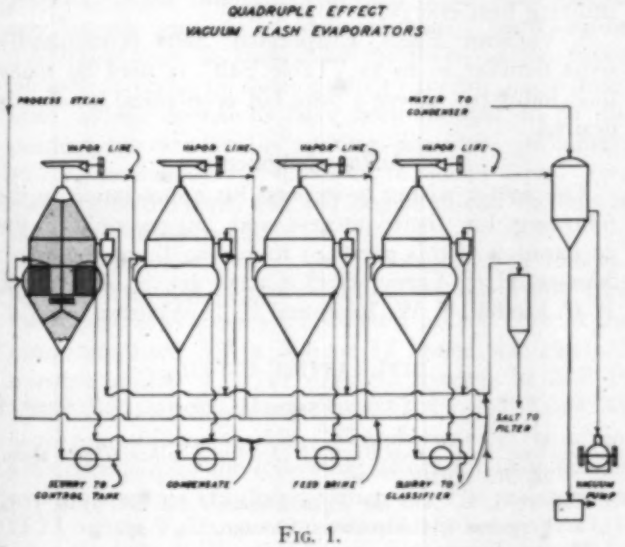


FIG. 1.

pressure so that the vapor formed by evaporation in the first kettle may be passed to the steam belt of the second which is hot enough to boil brine in the second; vapor from the second is used to boil brine in the third, and vapor from the third to boil brine in a fourth kettle. We see that by use of this arrangement, low pressure steam need be supplied to only the first kettle.

When four kettles are used in this manner, and operated as a unit, it is known as a quadruple effect. Most salt plants today operate either a quadruple or a triple effect. With such an arrangement as a multiple effect vacuum kettle system, each kettle acts not only as an evaporator, but also as a boiler producing heated vapor or steam for boiling the brine in the next succeeding kettle and as a condenser for the kettle immediately preceding. Reduced pressure on the brine in the last kettle of the effect is accomplished by passing the vapor into a dry vacuum pump and by use of a barometric condenser.

With the open pan process, the heated vapor containing a considerable quantity of heat units, is entirely lost, but in the vacuum kettle process in multiple effect, the hot vapor is used to the maximum efficiency. This is very important in view of modern day uncertainties regarding the fuel costs and labor conditions.

Turning now to a more detailed study of the construction of vacuum kettles note the first effect in Figure 1. The majority of salt vacuum evaporators or kettles are from 14 to 30 feet in diameter. They are cone shaped on the bottom and top, with the steam belt placed in a cylindrical portion between the cones, and may measure about 50 feet from cone tip to tip. The steam belt consists of several hundred copper tubes five feet long and 2½ inches in diameter, but the center is left open with a circular shaped chamber, known as a well, which is about six feet in diameter. A large impeller blade is placed a few inches below the bottom of the well and brine is circulated downward through the well and up through the tubes, which are surrounded by steam in the steam belt. Brine is carried only a few inches above the top flue sheet. Heat is transferred through the tube walls to brine and flash evaporation occurs at the surface of the brine. Due to vigorous agitation from the impeller, and boiling, the crystals of salt do not have an opportunity to cling together. They pass with the down flow of brine through the well and drop into a leg at the bottom of the kettle for removal to be washed, filtered, dryed and screened. Evaporation of water, removal of salt from the kettle and flow of brine into the kettle is continuous in operation.

### General

Under pressure of one atmosphere brine normally boils at about 226° F. (108° C.), but in the fourth kettle of a quadruple effect it may boil as low as 110° F. (43.3° C.). Table 4 is presented as an example of the

TABLE 4 *(6)*

*Temperature—Pressure Relationship—Quadruple Effect*

Vacuum Flash Evaporators

(Steam pressure to first effect 19.7 lbs. absolute)

| Kettle | Temperature of Steam in belt | Dome condition | | Effective temperature of saturated steam in dome available for steam belt of next kettle (less super heat) | Boiling point of Brine and temperature of super heat saturated steam |
|---|---|---|---|---|---|
| | | Inches Mercury-Vacuum | Inches Mercury-Absolute Pressure | | |
| 1 | 227° F. | 7.5 | 22.5 | 198° F. | 214° F. |
| 2 | 198° F. | 17.5 | 12.5 | 170° F. | 185° F. |
| 3 | 170° F. | 23.5 | 6.5 | 144° F. | 157° F. |
| 4 | 144° F. | 28.0 | 2.0 | 100° F. | 110° F. |

temperature and pressure relationship in operation of a quadruple effect. Let us assume that the steam to the first effect is exhaust steam from a turbine generator, Topping type, and is delivered to the steam belt of the first kettle at 5 pounds pressure. The temperature of this steam is 227° F., about the boiling point of saturated brine at one atmosphere pressure, but since the brine in the first effect is under a pressure somewhat less than this, it boils quite vigorously.

In contrast a battery of six open pans, each 150 feet long and 18 feet wide may produce in 24 hours operation 75 tons of grainer salt and approximately 400,000 pounds of water vapor containing tremendous quantities of heat units, but this is all discharged to the atmosphere and lost. A triple effect of 20 ft. vacuum flash evaporators may produce eight times this quantity of granulated salt. Incidental to the production of 600 tons of salt, there would be produced approximately 350,000 gallons of distilled water. Of this amount one-third will be sacrified through the barometric condenser thereby maintaining the partial vacuum in the system, but the heat contained in the vapor has been efficiently utilized and the remaining by product distilled water has important uses, among which is for boiler feed water.

Relative steam consumption and salt production for open pan and multiple effect flash evaporation systems are shown in Table 5:

TABLE 5

*Production of Salt Versus Steam*

| Method | Steam Per Hour | Salt Per Hour | Pounds Steam Consumption per Pound Salt |
|---|---|---|---|
| Grainer Pan | 29,000 | 5,800 | 5.00 |
| Vacuum Flash Evaporator, Double Effect | 46,600 | 26,400 | 1.77 |
| Vacuum Flash Evaporator, Triple Effect | 32,718 | 24,600 | 1.33 |
| Vacuum Flash Evaporator, Quadruple Effect | 21,400 | 23,000 | .93 |

We have pointed out that the final grain structure of salt, although basically cubic, is determined in its final arrangement or grouping of these cubes, by the process of evaporation. The shower of crystals known as vacuum or granulated salt formed by vacuum flash evaporative methods of production are tiny cubes, perfect in formation, and very uniform in size. They possess a fine luster and close, even grain. Since vacuum evaporators work as a closed system throughout, contamination from dust or other sources cannot enter, so this method produces a very pure, high quality product.

Vacuum flash evaporated salt is prepared for the market by careful screening into suitable particle sizes. Since the particles are so uniform it is only necessary to grade Vacuum Flash Evaporated Salt into two or three sizes. Although some users may have preference to grainer or flake salt, believing that it has a slightly faster rate of solubility, the more economical vacuum flash evaporated salt may be used quite satisfactorily. A few extra turns is slight inconvenience for the economy resulting from the use of Vacuum Flash Evaporated Salt.

Vacuum Flash Evaporated Salt is the type most familiar to all of us because of its prevalent use as "table salt." Besides in the home, there are many important industrial applications, only a few of which we can mention here such as the manufacture of self-rising flour, meat packing industry, canning of fruit, vegetables and juices, pickling of olives and cucumbers, salting fish, making butter, cheese, the baking of bread and pastries, for water softener regeneration, the processing of leather, manufacture of soap, paper making, textile industry and many others.

We see that Salt is not "just salt" any more. It is a scientific product, manufactured by elaborate, and costly machinery, subject to laws and rules of the utmost exactness. The salt producers work ever to improve the product and services, in order to enable manufacturers that use salt to sell more of their product, at more profitable prices. The controlled grades, economically produced by the use of modern equipment are their contribution to this goal.

## Summary

1. Development of a salt industry in the United States has gone through many important changes.

2. Salt is obtained from our vast underground deposits by mining, either mechanically in solid form or hydraulically as brine.

3. Salt may be recovered in solid form from hydraulically mined salt by evaporation, two common methods being grainer (open) pan evaporation and flash evaporation. The evaporation of natural brine by solar heat is practiced to a certain extent.

4. Vacuum Flash Evaporation is highly efficient in utilizing heat energy.

5. Vacuum Flash Evaporated Salt (Granulated) most familiar to us as "Table Salt" is used by many food industries where a pure but economical product is desired.

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# Influence of Packing Conditions on the Process Requirements of Vacuum Packed Whole Kernel Corn[a]

W. H. WADE, D. V. ALSTRAND, H. A. BENJAMIN AND J. M. JACKSON
*General Research Laboratory, American Can Company, Maywood, Illinois*

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**Data are presented to show the effect of several variables on the rate of heat penetration in vacuum packed whole kernel corn. These include maturity of the corn, fill-in weight, volume of added brine, and vacuum at the time of processing.**

The vacuum packing of vegetables has come into extensive use since the invention of the method some 20 years ago. Vacuum packing of the yellow varieties of whole grain corn has met with particular success. In recent years approximately 40 percent of the entire whole grain style pack has been canned by this method. Essentially, the vacuum procedure is based on the principle that the creation of a high vacuum in the can permits the use of a minimum amount of added water or brine. This liquid, in the absence of other gases, can vaporize to carry the necessary sterilizing heat from the container surfaces to the food particles. This eliminates the need to fill the can with a brine to transfer heat rapidly to the kernels of corn. By affording the consumer a vegetable almost free of cooking liquid, vacuum packing facilitates the utilization of all the water soluble vitamins and minerals contained in the brine, a good share of which is often discarded from brine packed vegetables in the home preparation of canned food.

Wide variations have been encountered in heat penetration data when studying the processing of this product. Some differences in data occur from can to can among supposedly identical cans. Such minor differences may be caused by variations in the vapor convection paths in relationship to thermocouple location. Wider deviations have been thought to be dependent on variables in packing procedure including: (1) fill-in-weight, (2) quantity of added liquid, (3) maturity of the corn, and (4) degree of can vacuum at the start of the process.

The National Canners Association Research Laboratory Bulletin 26L (Sixth Edition, March 1946) lists the following processes for vacuum packed corn in the commonly used 307 x 306 or 12 ounce size can: 35 minutes at 250° F. (121° C.), 45 minutes at 245° F. (118° C.) and 55 minutes at 240° F. (116° C.). A qualifying statement adds: "The processes given above are dependent on the following factors for maintenance of their intended sterilizing value: (a) The maintenance of 23 inches of can vacuum immediately before processing; (b) The presence of at least one ounce of free liquid; (c) The control of fill-in weight not to exceed 11¼ ounces of washed corn." Although these processes and specifications have given commercially satisfactory results, the specified conditions have necessarily been set rather arbitrarily. Thus it appeared worthwhile to give further study to the effects of vacuum, added liquid and fill-in weight in addition to the more elusive factor of corn maturity.

In the studies reported here, heat penetration tests were made using varying fill-in weights of corn in 307 x 306 size cans for each of three maturities of corn; namely, young corn, corn of average maturity, and mature corn. It is understood that these are purely arbitrary designations for different maturities of succulent corn as is generally produced for canning purposes. The corn used was a special hybrid Golden Cross variety.

Two approaches were used in the study of the effect of can vacuum on the rate of heat penetration in whole grain corn. One approach was to study the rate of heat penetration in cans closed at varying degrees of vacuum and processed immediately. A second approach was to close the cans at maximum vacuum and vary the holding times and holding conditions, thereby causing a lower can vacuum at processing time as a result of the release of gases from the raw corn by enzymatic action.

TABLE 1

*Moisture Content by Modified Brown-Duvel Method and from Alcohol Insoluble Solids (A. I. S.) Tests*

| Run No.[b] | Date Run | Alcohol Insoluble Solids (percent in canned sample) | Moisture from Kramer & Smith A. I. S. (percent) | Moisture Brown-Duvel (percent in raw corn) | Maturity |
|---|---|---|---|---|---|
| 6a | 8/28/47 | 17.5 | 73.7 | 74.0 | |
| 15c | 9/3/47 | 16.4 | 75.3 | 73.5 | |
| 20 | 9/5/47 | 15.8 | 76.4 | 76.0 | |
| 14c | 9/3/47 | 15.9 | 76.2 | 73.5 | |
| 27g | 9/12/47 | 15.5 | 76.9 | 76.5 | |
| 10 | 8/29/47 | 18.1 | 72.9 | 75.0 | Young |
| 19 | 9/5/47 | 16.8 | 74.7 | 76.0 | |
| 13c | 9/3/47 | 16.8 | 74.7 | 73.5 | |
| 28g | 9/12/47 | 15.0 | 77.9 | 76.5 | |
| 7a | 8/28/47 | 17.0 | 74.4 | 74.0 | |
| 3 | 8/26/47 | 17.5 | 73.7 | 75.0 | |
| 4 | 8/26/47 | 20.7 | 69.4 | 71.5 | |
| 17d | 9/4/47 | 20.1 | 70.2 | 69.5 | |
| 1 | 8/22/47 | 19.4 | 71.2 | 71.5 | |
| 8b | 8/28/47 | 22.4 | 67.1 | 68.0 | |
| 12 | 9/2/47 | 20.6 | 69.6 | 69.5 | Average |
| 2 | 8/22/47 | 20.7 | 69.5 | 71.0 | |
| 38 | 9/17/47 | 19.8 | 70.6 | 66.5 | |
| 5 | 8/27/47 | 21.3 | 68.6 | 69.0 | |
| 9b | 8/28/47 | 21.8 | 67.9 | 68.0 | |
| 16d | 9/4/47 | 21.2 | 68.7 | 69.0 | |
| 34j | 9/17/47 | 23.2 | 66.1 | 66.5 | |
| 35j | 9/17/47 | 24.2 | 64.9 | 66.5 | |
| 33i | 9/16/47 | 24.5 | 64.6 | 66.5 | |
| 24f | 9/9/47 | 22.9 | 66.5 | 68.0 | |
| 22e | 9/9/47 | 21.9 | 67.6 | 67.5 | |
| 18 | 9/4/47 | 25.2 | 63.8 | 68.5 | |
| 37 | 9/17/47 | 22.8 | 66.6 | 66.5 | Mature |
| 32i | 9/16/47 | 23.9 | 65.2 | 66.5 | |
| 23f | 9/9/47 | 23.5 | 65.7 | 68.0 | |
| 21e | 9/9/47 | 22.7 | 66.7 | 67.5 | |
| 26 | 9/11/47 | 24.4 | 64.7 | 69.0 | |
| 31i | 9/16/47 | 24.5 | 64.6 | 66.5 | |
| 30h | 9/15/47 | 23.4 | 65.8 | 68.0 | |
| 29h | 9/15/47 | 23.2 | 66.1 | 68.0 | |

[b] Letters in run number column indicate runs made from same batch of corn, e.g. 6a and 7a were from the same batch of corn, runs 13c, 14c and 15c were from another batch of corn, etc.

[a] Presented before the Ninth Annual I. F. T. Convention, San Francisco, Calif., July 13, 1949.

### Corn Maturity Tests

Maturity of the corn was judged by moisture tests made using a modified Brown-Duvel moisture determination method. These values were confirmed later by alcohol-insoluble solids determinations upon companion samples. The data of Kramer and Smith *(2)* were used to check the moisture values against alcohol-insoluble solids and, with only a few exceptions, the moisture values checked within 2 percent. The alcohol-insoluble solids data for tests made in 1947 and corresponding percentages of moisture as interpolated from the Kramer and Smith data, are shown in Table 1 along with values obtained by the modified Brown-Duvel method.

Corn of the following moisture contents was sought as being representative of the maturities desired for this particular hybrid corn:

| Designation of Corn Maturity | Moisture Content, Percent |
|---|---|
| Young | Greater than 73 |
| Average | 68-73 |
| Mature | Less than 68 |

### Heat Penetration Testing Procedure

Each heat penetration run consisted of nine cans in which the thermocouples were located in the geometrical centers of the cans. The selected corn was cut on a rotary cutter, washed by flotation, drained, and the cans hand filled to the desired fill-in weight. In all tests made except those to show the effect of can vacuum, three fill-in weights of corn were used. These were 10 ounces (284 grams), 11¼ ounces (318 grams) and 12½ ounces (354 grams). Careful filling and heavy pressing was necessary to obtain the 12½ ounce fills of corn. This fill would not be practical with present mechanical filling equipment, and was included only to exaggerate any effect of overfilling on the rate of heat penetration. Brine variables from none to 60 milliliters were used in increments of 15 milliliters for each of these fill-in weights and for each of the three maturities used.

The cans were closed at the desired vacuum using a semi-automatic vacuum closing machine. In all runs the cans were closed under 26 inches (66 cm.) of machine vacuum and were held 15 minutes before processing unless otherwise specified. All cans were water cooled after processing and vacuum readings were then made. Any can which had a substantially lower vacuum than control cans processed with the heat penetration cans was assumed to have a leaky thermocouple fitting and the data from such a can were rejected. Time and temperature relationship data from the slowest heating can having satisfactory vacuum in each run were used for calculation of the sterilizing value of a given process by the method of Ball *(1)*, with slight modification. The control samples, similarly packed and processed, were examined for headspace, drained net weight, and the amount of free liquid after processing.

To show the effect of varying the closing vacuum, corn of average maturity was used. A fill-in weight of 11⅛ ounces (315 grams) of corn plus 45 milliliters of added liquid was used in all cans in order to obtain a final product having approximately 11¼ ounces (318 grams) of drained corn plus 40 milliliters of drained liquid. Cans were closed at vacuums of 5, 10, 15, 20, and 26 inches (12.7, 25.4, 38.1, 50.8 and 66 cms.) of mercury and were processed immediately.

Both young and mature corn were used in the tests designed to show the effect of varying the can vacuum by varying the holding time and holding temperature of closed cans. These maturity extremes of the raw product were used to see if there was any great variation in their enzymatic production of gas and if any resulting significant reduction in the degree of vacuum existing at the beginning of the process would lower the sterilizing values obtained. Fill-in weights of 11¼ ounces (318 grams) of young corn plus 40 milliliters of added liquid and of 10¾ ounces (305 grams) of mature corn plus 55 milliliters of added liquid were used. Previous tests had shown that these fill-in weights and liquid additions, for the maturities specified, would give a drained weight of approximately 11¼ ounces (318 grams) plus approximately 40 milliliters of drained liquid. The cans were closed under 28 inches (71 cms.) of vacuum. Closed cans of young corn were held for ½ hour, 1 hour, and 1½ hours at 70° F. (21° C.) in water and for the same periods of time in water at 100° F. (38° C.). An additional test was made holding the closed cans in air at 96-98° F. (35.5-36.5° C.). This test was made to obtain results using more practical commercial conditions than holding in water. Holding closed cans in water at elevated temperatures would be expected to give extreme results as the rate of heat transfer between metal and water is greater than that between metal and air. Tests using mature corn were made only on samples held at 70° F. (21° C.) in water for the specified holding times.

### Results

*The Effect of Fill-In Weight.* The data in Table 2 definitely show a decrease in the sterilizing values obtained with increased fill-in weights of corn, other conditions being constant. The maximum difference in the sterilizing values, obtained when the fill-in weight

TABLE 2

*Relation of Fill Weight, Maturity, and Added Liquid to Heat Penetration in Vacuum Packed Whole Kernel Corn*
(307 x 306 Cans)

| Fill Oz. Av. | Added Liquid Ml. | Sterilizing Value ($F_o$) for 35 Minutes at 250° F. (121° C.) | | |
|---|---|---|---|---|
| | | Young Corn | Average Corn | Mature Corn |
| 10 | 0 | 11.3 (6) | 10.2[c] | 9.9 (34) |
| 10 | 15 | 14.5[c] | 11.4[c] | 9.5 (35) |
| 10 | 30 | 12.0 (15) | 14.2 (4) | 9.4 (33) |
| 10 | 45 | 13.2 (20) | 14.6 (17) | 11.2 (24) |
| 10 | 60 | 15.2 (14) | 13.5 (1) | 12.0 (22) |
| 11¼ | 0 | 4.2 (27) | 5.3[c] | 9.9 (18) |
| 11¼ | 15 | 9.1[c] | 9.0[c] | 7.5 (37) |
| 11¼ | 30 | 6.1 (10) | 7.5 (8) | 9.5 (32) |
| 11¼ | 45 | 8.5 (19) | 9.4 (12) | 6.9 (23) |
| 11¼ | 60 | 10.1 (13) | 11.0 (2) | 11.7 (21) |
| 12½ | 0 | 1.6 (28) | 1.4[c] | 1.5 (26) |
| 12½ | 15 | 6.9[c] | 3.0 (38) | 3.5[c] |
| 12½ | 30 | 2.1 (7) | 6.5 (5) | 2.9 (31) |
| 12½ | 45 | 4.4[c] | 7.3 (9) | 7.1 (30) |
| 12½ | 60 | 7.1 (3) | 10.7 (16) | 9.0 (29) |

[c] Tests made in 1948—all others made in 1947.

NOTE: Figures in parenthesis refer to run number for comparison with Table 1.

was varied from 10 to 12½ ounces (284 to 355 grams) was obtained with young corn and using 30 milliliters of added liquid. Under these conditions the $F_o$ value decreased from 12 to 2.1. The minimum difference in sterilizing value, with respect to fill-in weight increases, was with corn of average maturity and the use of 60 milliliters of added liquid. With these conditions the $F_o$ value decreased from 13.5 to 10.7. It is obvious that other factors are very closely related to the sterilizing values obtained with over filled cans. However, the general conclusion that increasing the fill-in weight decreases the sterilizing value of a given process, when other conditions are similar, seems justified. In the discussion of other factors studied, their relationship to overfilled cans will be pointed out.

One effective factor not studied, that of season to season variation in the raw corn, became evident when analyzing the results of the experiments. As it was not possible to complete the full series of tests in 1947, some were made during the 1948 canning season. These are designated with asterisks in Table 2. A comparison of the effect of the three variables used between the tests made in 1947 and 1948 cannot well be made without bringing in this season to season variable. It is not unreasonable to expect a seasonal variation in the physical characteristics of the same hybrid of corn, and in this case it was probably caused by differences in the weather of the two growing seasons. For example, in the particular locality in which the corn was grown the 1947 season was very hot and dry and the corn matured very rapidly, while the 1948 season was unusually cool with much rainfall. In handling the corn it was obvious that the 1947 corn, harvested to have a moisture content greater than 73%, was much smaller in kernel size, was softer and contained more kernel pieces and chaff, and in general was more difficult to wash. It is reasonable to expect that this corn would pack more tightly than the fully developed kernels of the ears of the 1948 season, even though the corn was harvested to have the same moisture content. As shown in Table 2, in most cases the 1948 data appear to give greater sterilizing values than would be expected from inspection of the 1947 results, indicating that the season to season variation may cause changes in the rate of heat penetration equivalent to or in excess of that caused by other variables.

The effect of fill-in weight can be demonstrated in terms of the required process time as well as in terms of sterilizing value. This has been done in Table 3 for the selected conditions of young corn with fills of 11¼ ounces (318 grams) and 12½ ounces (354 grams). It will be noted that the data indicate that with 60 milliliters of liquid, the heavier fill could be compensated for by a five minute increase in process time. However, with only 30 milliliters of liquid a substantial increase in process was indicated if the fill was increased to 12½ ounces (354 grams). For reasons already mentioned, it is hardly permissible to include the one set of 1948 data in Table 3. However, most of the 1948 data give sterilizing values in excess of that expected from analysis of the 1947 data. This makes it probable that the included data on 12½ ounces (354 grams) of young corn plus 45 milliliters of added liquid give a calculated equivalent process time on the low side.

TABLE 3

*Relation of Fill Weight to Calculated Equivalent Process Time for Young Corn*

| Added Liquid Ml. | Fill Oz. Av. | $F_o$ | Calculated Process Times at 250° F. Minutes |
|---|---|---|---|
| 30 | 11¼ | 6.1 | 35 |
| 30 | 12½ | 6.1 | 52 |
| 45 | 11¼ | 8.5 | 35 |
| 45 | 12½ | 8.5 | 45[a] |
| 60 | 11¼ | 10.1 | 35 |
| 60 | 12½ | 10.1 | 40 |

[a] Test made in 1948—all others made in 1947.

*The Effect of Added Liquid.* When the data in Table 2 from tests made in either 1947 or 1948 are viewed alone, in nearly all cases increasing the amount of added liquid increases the sterilizing value of a given process, when the other factors remain the same.

The greatest change caused by increasing the volume of added liquid occurred with cans filled with 12½ ounces (354 grams) of corn. Apparently, added liquid was more effective in increasing the sterilizing value in cans in which the corn was tightly packed.

*The Effect of Maturity.* From the data shown in Table 2, there appears to be little or no correlation between maturity and sterilizing value when other factors are constant. However, practical canning conditions dictate different fills and quantities of added liquid for the different maturities, and these factors have been shown to have a significant effect on heat penetration. In Table 4 are shown ratios of the drained free liquid to added liquid for the different maturities of corn used. Older corn absorbs more moisture than does younger corn, as is indicated by the data in Table 4, and so requires a higher ratio of liquid to corn. The customary practice is to fill less corn and add more liquid to the more mature product. Since decreased fill-in weights

TABLE 4

*Relation of Corn Maturity to the Ratio of Drained Liquid to Added Liquid*

| Corn Maturity | Fill In Weight (Av. Oz.) | Added Liquid (Ml.) | Ratio of Drained Liquid to Added Liquid * | Average of Ratios for Maturities Used |
|---|---|---|---|---|
| Young | 10 | 30 | 1.17 | |
| Young | | 45 | 1.09 | |
| Young | | 60 | 0.95 | |
| Young | 11¼ | 30 | 0.73 | |
| Young | | 45 | 0.98 | |
| Young | | 60 | 0.98 | .98 |
| Average | 10 | 30 | 0.97 | |
| Average | | 45 | 0.93 | |
| Average | | 60 | 0.78 | |
| Average | 11¼ | 30 | 0.97 | |
| Average | | 45 | 0.93 | |
| Average | | 60 | 0.70 | .88 |
| Mature | 10 | 30 | 0.60 | |
| Mature | | 45 | 0.78 | |
| Mature | | 60 | 0.82 | |
| Mature | 11¼ | 30 | 0.83 | |
| Mature | | 45 | 0.76 | |
| Mature | | 60 | 0.93 | .79 |

* Represents the average results obtained from drained weight tests on nine cans of each variable. All samples from 1947 season's pack.

and increased added liquid have been shown to increase the sterilizing value of any given process, the packing of older corn does not present the same hazard of under-sterilization as young corn if these adjustments are made.

*The Effect of Vacuum.* The results of the slowest heating can at each vacuum level used are given in Table 5. It is apparent that increasing the degree of closing vacuum increases the rate of heat penetration within the limits tested.

TABLE 5

*The Effect of Varying Closing Vacuum* [f]

| Closing Vacuum (In.) | Vacuum 24 Hours After Processing (In.) | $F_o$ for Process of 35 Min. at 250° F. |
|---|---|---|
| 5 | 2 | 4.0 |
| 10 | 4½ | 4.5 |
| 15 | 6½ | 6.0 |
| 20 | 10½ | 9.1 |
| 26 | 13 | 13.5 |

[f] All tests made in 1948.

Results showing data of the slowest heating cans obtained when vacuums were varied by varying the holding time of the closed cans before processing are shown in Table 6. Holding young corn at 70° F. (21° C.) for extended periods of time up to 1½ hours after closing did not change appreciably the final vacuums or sterilizing values obtained when compared to closed cans held for 30 minutes before processing. At 100° F. (38° C.) in water, however, there is some indication that even a ½ hour hold before processing affects the can vacuum and possibly the sterilizing value of the process. A one hour or longer hold in water at 100° F. definitely has a reducing effect on both can vacuum and sterilizing value for young corn. A 1½ hour hold in air at 96-98° F. reduced the vacuum, but a corresponding reduction in sterilizing value was not noted.

For mature corn held at 70° F. in water there is a downward trend in can vacuum and sterilizing value as the cans are held from ½ to 1½ hours, but the effect is slight and may not be significant.

## Summary

In general it was found that increasing the fill-in weight of corn, or decreasing the volume of added liquid, decreased the sterilizing value of any given process. The greatest effect of maturity of the corn is that it requires changing factors such as the fill-in weight and volume of added brine which in turn affect the sterilizing value obtained with a given process. Cans closed with varying degrees of vacuum and processed immediately show that the sterilizing value obtained with a given process is decreased markedly when the vacuum of the processed can is less than 10 inches of Hg. 24 hours after processing. Contrary to expectations, closed cans of vacuum packed corn held for 1½ hours in air at 96-98° F. (35.5-36.5° C.) before processing showed a rate of heat penetration similar to comparably prepared cans processed immediately in spite of a slight decrease in the vacuums of the "held" cans. However, cans held in water at 100° F. showed increasing reduction in vacuum with holding time, and, consequently, serious loss of sterilizing value of the process for the longer holding periods.

## Acknowledgment

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TABLE 6

*Effect on Heat Penetration of Varying Vacuum by Varying Holding Time and Holding Conditions of Closed Cans Before Processing* [i]

| Corn Maturity | Holding Time (Hrs.) | Holding Temp. (° F.) | Initial Temp. (° F.) | Holding Media | Vac. at [g] Start of Process (In. Hg.) | Vac. After [h] 24 Hours (In. Hg.) | $F_o$ for Process of 35 min. at 250° F. |
|---|---|---|---|---|---|---|---|
| Young | ½ | 70 | 70 | Water | 21½ | 17½ | 10.3 |
| Young | 1 | 70 | 72 | Water | 20 | 15 | 8.8 |
| Young | 1½ | 70 | 70 | Water | 20½ | 17 | 10.0 |
| Young | ½ | 100 | 90 | Water | 18 | 13½ | 9.7 |
| Young | 1 | 100 | 98 | Water | 15½ | 13 | 4.9 |
| Young | 1½ | 100 | 94 | Water | 9½ | 6½ | 5.3 |
| Young | 1½ | 96-98 | 84 | Air | 16 | 14½ | 10.9 |
| Mature | ½ | 70 | 64 | Water | 22½ | 19½ | 13.7 |
| Mature | 1 | 70 | 69 | Water | 21 | 17 | 12.8 |
| Mature | 1½ | 70 | 70 | Water | 19 | 15½ | 12.4 |

All cans were closed with 28 inches (71 cm.) of vacuum.

[g] The vacuums listed in this column are the average of two cans and were measured on cans filled simultaneously with and similar to the heat penetration cans except thermocouples were not used.

[h] Vacuums listed in this column were measured on the same cans as were used to establish the heat penetration curve for the condition involved.

[i] All tests made in 1948.

# Preservation of Colour in the Milling of Apples for Natural Apple Juice[a]

F. E. ATKINSON AND C. C. STRACHAN

*Fruit and Vegetable Products Laboratory, Dominion Experimental Station, Summerland, B. C.*

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**This investigation includes a comparison of methods of preventing oxidation in the milling of apples for natural apple juice. Nitrogen and carbon dioxide gas have been used alone and in combination with varying amounts of ascorbic acid. The results are compared with those obtained when ascorbic acid alone was used, as in the commercial procedure. Nitrogen and carbon dioxide gas each have been found to exert some benefit, nitrogen being preferred to carbon dioxide. It may be possible to use nitrogen by itself or with markedly reduced amounts of ascorbic acid.**

In the production of natural apple juice, an effort is made to maintain the maximum natural flavour and colour of the apple. In the process as commercially employed at the present time, natural colour and flavour are maintained by the use of ascorbic acid to prevent oxidation. Ascorbic acid is atomized in the mill in a concentrated liquid form. The minimum amount usually required with apples of good condition is 20 mg. per 100 g. When the concentration exceeds 30 to 35 mg., the operation is not considered economically feasible. Besides the cost of adding this expensive chemical, there is also difficulty in maintaining an even flow into the mill because of possibilities of the atomizers clogging or the pump failing. Also, chemical control is necessary, as the amount of ascorbic acid required for this purpose differs with the variety and maturity of the apples being milled. It has been found that at least 1 mg. of ascorbic acid per 100 ml. should be in the extracted juice from the presses *(1)*. In order to overcome these difficulties in operation and cost, experiments were undertaken to demonstrate the feasibility of other methods.

## Experimental

Apples were milled in an atmosphere of nitrogen alone and of carbon dioxide alone, and each of these gases was used in the mill with 5, 10, 15, and 20 mg., respectively, of ascorbic acid per 100 g. of fruit. The same procedure was used to mill apples in an atmosphere of air with 5, 10, 15, 20, 25, 30, 40, 50, and 60 mg., respectively of ascorbic acid. Nitrogen gas also was diluted with 25, 50, and 75 percent of air, and the apples were milled in this atmosphere without ascorbic acid. Blanks were milled in air.

In the physical operation of this project, McIntosh apples that had been stored for 7½ months at 32° F. (0° C.) were used. In the preparation of a sample, the apples were first diced into ⅜-inch cubes with an Urschel strip cutter and dicer. The cubes were accumulated in water containing Aerosol, to facilitate the removal of occluded air. Each sample was freshly cut and prepared as quickly as possible. A 300-g. amount of the diced apples was placed in the jar of an Oster mixer, and the jar was completely filled with recently distilled water. The fruit was agitated to remove any adhering air bubbles, and the jar was again filled brimming full. The jar was then sealed and inverted in a pan of water, where the seal was removed and nitrogen or carbon dioxide gas introduced to replace part of the water in the jar until 200 ml. remained with 300 g. of apple. This created a gas volume of 500 ml. When ascorbic acid was added, this was introduced through a water-sealed tube onto the surface of the diced fruit in the jar. The sample was then blended for 15 seconds.

Following blending, a gas analysis was made with a Lunge nitrometer, to determine the carbon dioxide and the oxygen released. Each sample was then placed in a 100-ml. graduate for observation after standing 20 minutes. As the preparation of a sample required from 8 to 10 minutes, the elapsed time from cutting of the fruit to final observation was approximately one-half hour.

## Results

*Gas Analysis.* Analysis of the gas in the blender after the sample was blended in an atmosphere of 100 percent nitrogen indicated an oxygen content of from 2 to 2.3 percent and a carbon dioxide content of from 0.5 to 0.6 percent (nitrogen blank maximum 0.4 percent oxygen). The oxygen in the atmosphere was naturally present in the fruit tissue, and in a 500-ml. volume of gas it would be capable of destroying from 70 to 150 mg. of ascorbic acid if oxidation were complete *(2)*.

*Effect of Varying Atmospheres and Ascorbic Acid on Colour.* Samples milled in air were markedly brown in 5 minutes. Samples with carbon dixoide or nitrogen alone were browned in 20 minutes to the maximum amount permitted for commercial operation. Juice containing 10 mg. of ascorbic acid with either carbon dioxide or nitrogen was sufficiently white for satisfactory commercial operation. With ascorbic acid alone, browning was marked in from 5 to 10 minutes until concentrations of 40 mg. were reached. The samples containing ascorbic acid concentrations of 40 and 50 mg. were on the borderline (Figures 1, 2, and 3). These high concentrations of ascorbic acid were necessary with this fruit, as it had been stored for a considerable time and was past its optimum condition for the manufacture of natural apple juice. However, it is interesting that such a high concentration of ascorbic acid was needed when this constituent was used alone, whereas when it was used in combination with nitrogen or carbon dioxide, it could be reduced to 10 mg. or possibly eliminated.

[a] Presented before the Ninth Annual I. F. T. Convention, San Francisco, Calif., July 14, 1949.

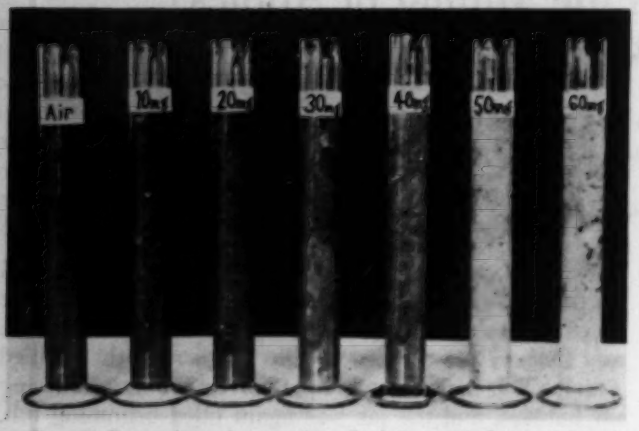


FIG. 1. Browning of natural apple juice as influenced by air and ascorbic acid.

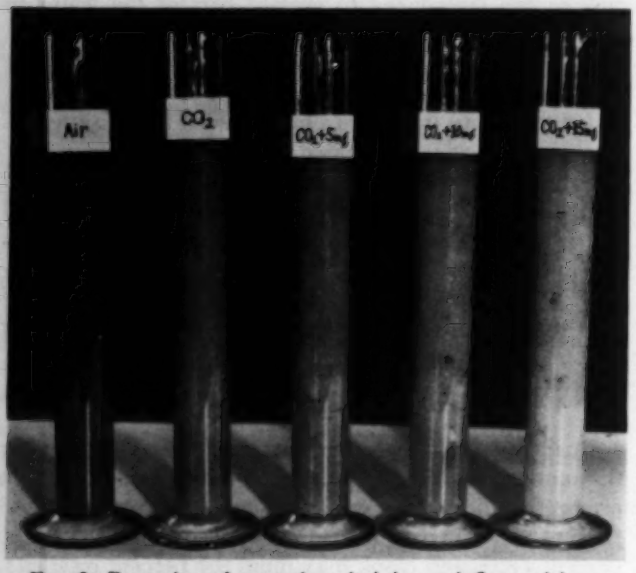


FIG. 2. Browning of natural apple juice as influenced by carbon dioxide and ascorbic acid as compared with air.

A milling atmosphere containing 75 percent of nitrogen and 25 percent of air retarded oxidation to approximately the same extent as air and 40 to 50 mg. of ascorbic acid per 100 g. The colour of samples milled in an atmosphere containing 50 percent of nitrogen was similar to that of samples treated with about 40 mg. of ascorbic acid per 100 g. The colour of samples milled in

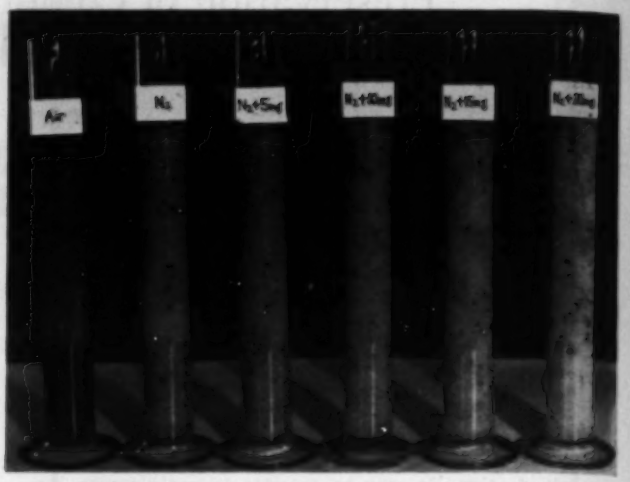


FIG. 3. Browning of natural apple juice as influenced by nitrogen and ascorbic acid as compared with air.

an atmosphere containing 25 percent of nitrogen was similar to that of samples milled in air and treated with from 25 to 30 mg. of ascorbic acid per 100 g.

Further experiments were conducted to determine if the reaction between ascorbic acid and oxygen contained in the milling gas was uniform in all cases. For this latter test, apple juice was pressed and heated to 99° F. (37° C.). Sufficient ascorbic acid was added to give a content of 50 mg. per 100 ml. of juice. A 500-ml. portion of this juice was then blended for 30 seconds with 450 ml. of gas as follows: (1) air, (2) nitrogen, (3) 75 percent of nitrogen and 25 percent of air; (4) 50 percent of nitrogen and 50 percent of air, and (5) 25 percent of nitrogen and 75 percent of air. Results of these tests are shown in Table 1. It will be noted that the ratio of the loss of ascorbic acid (in milligrams) to the oxygen (in millilitres) in the blending atmosphere is fairly constant, varying from 1:9.7 to 1:11.3, irrespective of the atmosphere. It would appear from these tests that the exclusion of air is the main factor in preventing oxidation.

*Nitrogen versus Carbon Dioxide.* Carbon dioxide seems to give the pulp a greyish appearance, and considerable carbon dioxide dissolves in the juice of the apple during the milling operation. Consequently when this juice is pressed and later deaerated and sterilized, there is a tremendous evolution of gas which would

TABLE 1

*Ascorbic Acid Content of Apple Juice Blended in Varying Atmospheres of Air and Nitrogen at 99° F. (37° C.)*

| Lot No. | Ascorbic Acid Content of Juice (mg./100 g. | | Loss of Ascorbic Acid | | Atmosphere | Oxygen (ml.) in Blending Atmosphere | Ratio of Ascorbic Acid Loss (mg.) to Oxygen (ml.) in Blending Atmosphere |
|---|---|---|---|---|---|---|---|
| | Original | After 30 min. | mg./100 g. | % | | | |
| 1 | 48.6 | 38.9 | 9.7 | 20 | Air | 94.5 | 1:9.7 |
| 2 | 50.0 | 49.3 | 0.7 | 1 | $N_2$ | Natural $O_2$ content | |
| 3 | 50.0 | 47.9 | 2.1 | 4 | 25% air 75% $N_2$ | 23.6 | 1:11.3 |
| 4 | 49.3 | 44.5 | 4.8 | 10 | 50% air 50% $N_2$ | 47.2 | 1:9.8 |
| 5 | 51.0 | 44.7 | 6.3 | 12 | 75% air 25% $N_2$ | 70.8 | 1:11.2 |

overload the equipment unless it was built to take care of this extra gas load. There was no appreciable difference in the flavour of the juice whether made with carbon dioxide, nitrogen, or ascorbic acid.

*Commercial Adaptation of Results.* In the commercial adaptation of these findings, some modifications would have to be made in the equipment as used at present. It is common practice for apples to be conveyed either by water or by a slatted link belt conveyor to a point above the mill and for the apples to fall by gravity from the conveyor into the mill. This entails a large open throat on the top side of the mill to conduct the apples into this equipment. Where a gas-tight arrangement is necessary, it is thought that the gas tightness could be achieved by allowing the conveyor bringing apples to the mill to deliver them into a tank of water at a point lower than the throat of the mill. Then by having a gas-tight housing extending from the throat of the mill to below the surface of the water in the tank, a gas-tight condition could be developed. An elevator and conveyor could pick up the apples within the housing and carry them to the mill. A small flow of gas would be maintained through the mill to sweep away the 2 percent of oxygen released from the apples being milled.

At the present time, all natural apple juice produced for the Canadian market is fortified with ascorbic acid to a minimum of 35 mg. per 100 ml. of juice. Fortification of apple juice is not mandatory, and with the process outlined it may be possible to pack a type of natural juice with little or no ascorbic acid. If economic conditions necessitate the lowering of production costs, then the use of nitrogen and carbon dioxide as outlined in the foregoing may be the answer to this feature.

## Conclusion

Natural unfortified apple juice maintained in a white condition with nitrogen, carbon dioxide, and possibly small amounts of ascorbic acid, could compete successfully on a price level with clarified apple juice. This is due, first, to the fact that from 10 to 15 percent of apple juice being clarified is lost in the clarification process. Sometimes this loss is as high as 20 percent. Secondly, with the natural juice, no clarifying agent (such as Pectinol or tannin and gelatin) is necessary. Thirdly, the production of natural juice is a straight-line operation requiring no storage tank or extra labour for adding clarifying agents, filtering, or cleaning of storage tanks. In view of these advantages, it is thought that natural apple juice, in which the colour is kept white with nitrogen or carbon dioxide and probably a small amount of ascorbic acid, has considerable commercial possibilities.

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# Ammoniated Pectins

WILLIAM A. MITCHELL
*Central Laboratories, General Foods Corporation, Hoboken, New Jersey*

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**A number of reactions were carried out with several ammoniated pectins to obtain more information about their physical properties and about the structure by which nitrogen is held in the skeleton of the pectin molecule. The data support the hypothesis that an amide linkage accounts for the nitrogen not removed by acid washing of the ammoniated pectins.**

Although Carson *(2)* and Joseph, Kieser and Bryant *(4)* have recently reported a number of nitrogen-containing derivatives of pectin which have been described as amides, other workers *(6)* who have studied the reaction of the pectin or pectinic acids with ammonia have generally considered that the reaction products bind the nitrogen in the form of ammonium salts. Olsen and Stuewer *(5)* regarded their products from this standpoint. Evans and Huber *(3)* specifically assumed that in their deesterification of pectinic acid with ammonia they obtained the usual type of pectinic acid salt, but with less degradation of molecular weight than is normally caused by fixed alkalies. In view of the data reported herewith, it is probable that the material of their reaction also contained some nitrogen in a more stable combination, namely, the amide linkage.

Joseph, Kieser and Bryant *(4)* have reported on the amide linkage in the low equivalent weight pectins. It is the purpose of this paper to report a whole gamut of amide pectins having widely different nitrogen content and physical properties.

A number of reactions were carried out with ammoniated pectins in order to learn more about their properties and to elucidate more fully the structure by which the nitrogen is held in the skeleton of the pectin molecule. These reactions involved hydrolyses with sodium hydroxide to regenerate the ammonia, hydrolyses with 12.5 percent hydrochloric acid to decarboxylate the uronic acid residues, esterification with methanol, and exposure to pectinase to hydrolyze the the pectin chain. Of these, the recovery of ammonia and the decarboxylation of uronic acid radicals proceeded as would be expected of an acid amide structure. Under the experimental conditions used, the free carboxyl groups in the pectin molecule were esterified; no conversion of the presumed amide groups to ester groups took place. The ammoniated pectins also are only partially hydrolyzed by pectinase.

TABLE 1

*Time of Ammoniation [a] of Rapid Set Apple Pectin and Its Effect on the Chemical Analysis and Gel-Forming Properties*

| Sample and Time of Treatment | Equivalent Weight | Methoxyl by Saponif. percent | Galact. by Titration percent | Nitrogen Kjeldahl percent | Galact. tied up with Nitrogen percent | Total Galact. percent | Pectin in Gel. percent | pH of Gel. | Description |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 718-13 Rapid Set Pectin | | | | | | | | | |
| 0 Time | 627 | 9.35 | 85.2 | 0.012 | ..... | 85.4 | ½ | ..... | No gel. |
| 4 Hours | 614 | 6.19 | 66.7 | 1.74 | 21.7 | 88.4 | ½ | 2.80 | |
| | | | | | | | 1 | 3.02 | No gel or thickening. |
| 8 Hours | 568 | 4.12 | 56.3 | 2.52 | 31.5 | 87.8 | ½ | 2.87 | Thin and watery cloudy gel. |
| | | | | | | | 1 | 3.08 | Very weak,cloudy gel. |
| 16 Hours | 524 | 1.70 | 44.0 | 3.76 | 47.0 | 91.0 | ½ | 2.92 | Crystalline, weak, cloudy gel. |
| | | | | | | | 1 | 3.21 | Fairly strong, cloudy gel. |
| 24 Hours | 529 | 0.92 | 39.0 | 3.89 | 48.6 | 87.6 | ½ | 2.94 | Very weak gel, syneresis. |
| | | | | | | | 1 | 3.21 | Cloudy crystalline gel, syneresis. |

[a] The ammoniation was carried out with 20 g. of air-dried pectin placed on a watch glass in a desiccator at room temperature over 28 percent ammonium hydroxide. The percent galacturonide is calculated from the equation $(176\ N + 190\ S) \times 100 =$ percent galacturonide, in which N = equivalent of free carboxyl per gram and S = equivalent of esterified carboxyl per gram. In the case of the pectin amide, the equivalent is multiplied by 175. Total galacturonide is calculated from the equation $(176\ N + 190\ S + 175\ A) \times 100 =$ total galacturonide, in which A = equivalent of amide per gram.

As the jellying properties of ammoniated pectins are different from the usual pectins, the equivalent weight and ester content cannot be used to make a direct comparison between these two types of materials in relation to their commercial usefulness.

## Experimental

The ammoniation can be carried out directly with gaseous or liuid ammonia or with ammonium hydroxide dissolved in alcohol—such as 70 percent isopropanol. The degree of ammoniation depends, among other things, upon the available ester linkages and the time of exposure to the reagent.

The pectin-ammonia reactions reported here were carried out in one of two manners: (1) by exposing relatively dry pectin in a desiccator over 28 percent ammonia, and (2) by exposing relatively dry pectin to ammonia gas under pressure.

The gelling properties of the ammonium salts obtained were investigated. Gels were made by mixing 1 g. of the dry pectin and 1.5 g. of d-gluco-Δ-lactone, adding 97.5 ml. of water, and heating gently over a gas flame until a water-clear dispersion was obtained. The gels were allowed to stand overnight at 25° C. before being characterized.

The equivalent weight was obtained after thorough washing of the pectins with acid-alcohol, as suggested by Olsen et al. *(5)*. The methoxyl content was determined by saponification in 0.08 N sodium hydroxide for 15 minutes at room temperature. Moisture content of the samples was determined by drying them for 24 hours at 70° C. in about 28 inches of vacuum.

## Results

### *A. Analytical values for some ammoniated pectins.*

From Table 1, it will be noted that there is only a little decrease in the equivalent weight of the pectin with time of ammoniation. The values indicate that under these conditions there is little hydrolysis of the ester linkage.

The saponification titre decreases, which reflects corresponding decreases in the methoxyl content. This means that the ester linkage is being reduced without producing free carboxyl groups. Furthermore, from column 4, there will be noted a progressive apparent decrease in galacturonide content as time of ammoniation increases. These values are calculated from the acid and saponification titres of the pectin. From column 5, however, it is seen that the Kjeldahl nitrogen values progressively increase with time of ammoniation.

If one molecule of ammonia reacts with one ester group to form the amide, then the galacturonide values shown in column 6 are obtained for galacturonide tied up in the nitrogen linkage. It will be seen that these galacturonide values increase with time of ammoniation. Now if this galacturonide value is added to the galacturonide value obtained from the titration of the free carboxyl groups and the methoxyl groups, the values given in column 7 are obtained. The galacturonide value checks fairly closely with the value for the original Rapid Set Apple Pectin. From this, it is concluded that one molecule of ammonia reacts with one ester group.

Columns 8, 9, and 10 show the relative gelling ability of these ammoniated pectins. For this particular pectin, after 8 hours treatment with ammonia, an ammoniated pectin is produced that will give, under the conditions of testing, a weak gel with water at 0.5 percent pectin concentration. The 16-hour treatment produces a

TABLE 2

*A Comparison of the Calculated Nitrogen Values and Actual Kjeldahl Nitrogen Values of Some Ammoniated Pectin*

| Sample and Time of Treatment [b] | Apparent Galacturonide by Titration percent | Calculated Nitrogen [c] percent | Actual Kjeldahl Nitrogen percent |
|---|---|---|---|
| 718 Rapid Set Apple Pectin | | | |
| 0 Time | 88.3 | ..... | ..... |
| 4 Hours | 66.7 | 1.73 | 1.74 |
| 8 Hours | 56.3 | 2.56 | 2.52 |
| 16 Hours | 44.0 | 3.55 | 3.76 |
| 24 Hours | 39.0 | 3.94 | 3.89 |

[b] Treated in a desiccator at room temperature over 28 percent ammonium hydroxide solution.

[c] Computed by multiplying the difference in galacturonide value (initial value at 0 Time minus value after X hours of treatment) by 14/175. This assumes no loss in non-galacturonide material.

stronger gel, but the 24-hour treatment again produces a weaker gel.

In Table 2, data are given showing the difference in galacturonide obtained by titration of the pectins treated with ammonia for various times. If this difference is assumed to be due to the presence of galacturonamide polymer, the theoretical nitrogen can be calculated. It will be seen that the actual Kjeldahl nitrogen values check well with the values calculated from the apparent decrease in galacturonide.

*B. Reactions of ammoniated pectins.*

1. *Distillation of ammonia from ammoniated pectinic acid in sodium hydroxide solution.* Sample 779-61 was made from a Rapid Set Apple Pectin that contained 0.01 percent nitrogen. This pectin was ammoniated for 24 hours in a desiccator over 28 percent ammonia at room temperature. The Kjeldahl nitrogen on a dry pectinic acid basis, alcohol-acid washed, was found to be 3.89 percent (Table 3).

TABLE 3

*Recovery of Ammonia from Ammoniated Pectins by Distillation With Sodium Hydroxide*

| Sample of Ammoniated Pectin | Kjeldahl Nitrogen percent | Ammonia Nitrogen percent | Kjeldahl Nitrogen Recovered percent |
|---|---|---|---|
| 779-61 | 3.89 | 3.44 | 88.4 |
| 807-55-4 | 4.67 | 4.43 | 94.9 |

Sample 807-55-4 was made from a pectinic acid that was further esterified before the ammonia treatment. Sixty grams of Rapid Set Apple Pectinic Acid were esterified at room temperature by employing 750 ml. of methyl alcohol and 10 ml. of concentrated sulphuric acid and allowing the mixture to stand for 4 days at room temperature. The supernatant liquid was poured off, fresh alcohol and acid were added, and the mixture was allowed to react for 10 more days. The pectin was filtered and acid-alcohol washed. The acid-alcohol washed sample was treated at room temperature for one hour under 5-10 pounds pressure with ammonia gas. This sample contained 4.67 percent Kjeldahl nitrogen on a dry, free-acid basis.

Samples of these ammoniated pectins, each weighing 0.3 g., were placed in Kjeldahl flasks along with 500 ml. of 5 percent sodium hydroxide. A 400-ml. amount of liquid was distilled off into standard acid and the ammonia titrated.[d] An additional 400 ml. of water was added to the Kjeldahl flask and the distillation carried out a second time. This second distillation yielded no ammonia.

From Table 3, it will be seen that most of the nitrogen of these ammoniated pectinic acids can be recovered as ammonia. This supports the theory of amide linkage.

2. *Ammoniated pectin reacted with methyl alcohol (reversing the reaction).* Several attempts were made to react ammoniated pectins with methyl alcohol, employing various catalysts. The amide linkage was not replaced by ester groups, but many of the free carboxyl groups were esterified. Typical results were obtained by reacting 10 g. of ammoniated pectinic acid in 100 ml. of absolute methyl alcohol containing 5 ml. of concentrated sulphuric acid at reflux temperature for three hours.

From Table 4, it will be seen that there is an increase in the methoxyl value after the esterification treatment. Note, however, that the equivalent weight has increased, indicating that the free carboxyl groups were esterified. When the nitrogen values are considered, it will be seen that there is no great drop in nitrogen value to account for such a large increase in methoxyl value. Furthermore, in the case of the beet pectin, there is an actual increase in the nitrogen value. The reason for this increase in nitrogen becomes apparent when one looks over the galacturonide columns which show an increase in galacturonide for the samples that have been esterified. Non-galacturonide material has been removed in the esterification.

Because there has been such a small change in nitrogen value, which in the main can be accounted for by increase in methoxyl or increase in galacturonide, it must be concluded that there was but little reaction of the methyl alcohol with pectin amide and that the free carboxyl groups were being esterified.

3. *Reaction of ammoniated pectins with hot 12.5 percent hydrochloric acid (Tollens-Le Fevre Analysis).* As pectins split off carbon dioxide on treatment with boiling 12.5 percent hydrochloric acid, attempts were made to remove carbon dioxide after the same procedure from

[d] Note that the alkali concentration rises steadily to about 25 percent.

TABLE 4

*Reaction of Ammoniated Pectinic Acids with Methyl Alcohol (Esterification)*

| Sample [e] | Eq. Wt.[f] | Methoxyl by Titration percent | Galact. by Titration percent | Kjeldahl Nitrogen percent | Galact. Tied Up As Amide percent | Total Galact. percent |
|---|---|---|---|---|---|---|
| 779-83 Ammoniated lemon pectin | 395 | 5.74 | 79.7 | 0.56 | 7.0 | 86.7 |
| 703-108 Above pectin treated with methyl alcohol and sulphuric acid | 727 | 10.21 | 87.0 | 0.44 | 5.5 | 92.5 |
| 780-77 Ammoniated beet pectin | 663 | 0.26 | 28.1 | 2.09 | 26.1 | 54.2 |
| 703-103 Above sample treated with methyl alcohol and sulphuric acid | 4500 | 8.96 | 58.8 | 2.38 | 29.7 | 88.5 |

[e] These ammoniated pectins were obtained by treating lemon peel and beet pulp over 28 percent ammonium hydroxide in a desiccator at room temperature for 24 hours.

[f] These analytical values are on the pectinic acid basis.

TABLE 5

*Galacturonide Values by Titration and by Tollens-Le Fevre $CO_2$ Method*

| Sample of Pectin | Eq. Wt. | Uronic Anhydride [a] by Titration percent | Uronic Anhydride by $CO_2$ Method (4 hrs.) percent | Kjeldahl Nitrogen percent | Total Galac. from Titration plus Nitrogen Analysis percent |
|---|---|---|---|---|---|
| No. 2 ammoniated | 429 | 65.8 | 80.0 | 1.68 | 86.9 |
| No. 3 ammoniated | 436 | 61.3 | 71.7 | 1.55 | 80.6 |
| No. 8 not ammoniated | 301 | 83.5 | 77.8 | ..... | ..... |
| No. 10 not ammoniated | 282 | 82.2 | 75.0 | ..... | ..... |
| Galacturonic acid (dry acid basis)[b] | 194 | 95.8 | 96.2 | ..... | ..... |

[a] The uronic anyhydride is calculated on the basis of dry pectinic acid.
[b] The moisture in the dried acid was determined by titration with N/10 sodium hydroxide. This gave a value of 90.35 percent of dry galacturonic acid. The theoretical value for galacturonic acid in the monohydrate is 194/212 = 91.5 percent. It can be seen that there is slightly more water than the theoretical amount for forming the monohydrate.

the ammoniated pectins. Table 5 gives data collected by the Bryant and Joseph *(1)* modification of the Tollens-LeFevre method for determining the carbon dioxide given off by pectins.

It will be seen from Table 5 that carbon dioxide is given off from the amide pectins on heating with 12.5 percent hydrochloric acid. For the ammoniated pectins more uronide is obtained by the carbon dioxide method than by titration alone. However, when the carboxyl groups tied up with nitrogen are calculated and added to the titration value, then the carbon dioxide method gives the lower uronide value. Lower galacturonide values for the carbon dioxide method are also given for the non-ammoniated pectins. It is apparent that a 4-hour boiling time, under the conditions employed, was not long enough for these pectins, assuming the titration values to give the correct uronide content. Preliminary experiments have shown that a 5-hour boiling time gives much closer checks for these pectins, when one uses the titration method as a basis.

## Summary

1. Several pectins have been treated with ammonia, and it has been shown that ammonia reacts at the ester group of the pectin to form a rather stable linkage, probably the amide linkage.

2. Some of the class reactions of the amides have been tried with these ammoniated pectins. Some of these reactions support the hypothesis that an amide linkage accounts for the nitrogen that is not removed by acid washing of the ammoniated pectins.

3. Some of the physical properties of these ammoniated pectins are described.

4. Analytical data are presented to support the theory of amide linkage in these ammoniated pectins.

## Acknowledgment

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# Solution of Irish Moss Extractives by Acidulation[a]

LEONARD STOLOFF
*Krim-Ko Corporation, New Bedford, Mass.*

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**A technique for the preparation of Irish Moss Extractive solutions by adjustment of pH is described. The effects of pH, time, temperature and "retardents" on hydration of the extractive are described and interpreted.**

The physical condition and aesthetic quality of many of the food compositions we eat are dependent on those important ingredients, the stabilizers, whose nature and role have long been cloaked in mystery by the kitchen alchemist and the trade secret. The Oriental origin of many of the stabilizer materials does not detract from the air of mystery surrounding their use. Yet the merchandisability of many of our big volume food items depends on stabilizers.

Although several oil soluble stabilizers have entered the field of recent years, the most important group is the water soluble gums or hydrocolloids including gelatin, pectin, acacia, tragacanth, agar, algin and Irish Moss extractive. World War II, cutting off our imports, demonstrated our dependence on foreign sources for hydrocolloids, stimulated the exploitation and study of domestic raw materials and resulted in the development of a seaweed extractive industry based on Irish moss—*Chondrus crispus* to our botanical friends.

The processing problems which had restricted production and utilization of the Irish moss hydrocolloid have been overcome and a refined, easy-to-use extrac-

[a] Presented before the Ninth Annual I. F. T. Convention, San Francisco, Calif., July 11, 1949.

tive is now available in powder form from which water solutions are readily prepared by the use of heat.

Products already employing sizable quantities of extractive are chocolate milk, ice cream, milk puddings, baker's icings, albumin whips, fountain syrups and tooth-paste — to mention a few. Techniques have already been worked out for using extractive in water gel desserts, antioxidant dips, pie fillings, etc. However, for many purposes it is inadvisable to use heat and for many purposes a cold process results in production conveniences and economies. Therefore when it was observed that Irish moss extractives dispersed in vinegar gave brilliantly clear solutions, the broad field of the rôle of pH on the solubility and nature of Irish moss extractives was studied.

Our most important tools in this study were a Waring blendor, Beckman pH meter and a Brabender recording viscosimeter. The carriage of the viscosimeter was adapted to hold 250 ml. beakers. The general technique of observation was to disperse the powdered extractive into the desired aqueous medium in a Waring blendor and immediately transfer the mix to a beaker in the carriage of the viscosimeter where a viscosity-time record was obtained.

To determine whether the observed rapid solution was due to specific anions or was entirely a result of hydrogen ion concentration, a series of viscosity-time curves were made using five of the more commonly utilized mineral and organic food acids. These acids were all employed in 0.1 N solution. To obtain a series of solutions at different pH values, sodium hydroxide was added to these acid solutions in graded amounts. In this manner the concentration of the anion was kept constant. The extractive was added at a concentration of 2.00 percent. pH values were determined after the extractive had been dissolved since its incorporation would have some effect on the pH. The time required to attain maximum viscosity was determined and plotted against final pH for each acid. The resulting graph (Figure 1) indicates that the rate of water absorption is a function of pH and that for rapid absorption the final pH should be below 6.0 and preferably below 5.5.

Although the dispersions prepared by acidulation gave immediate evidence of solution by their clarity,

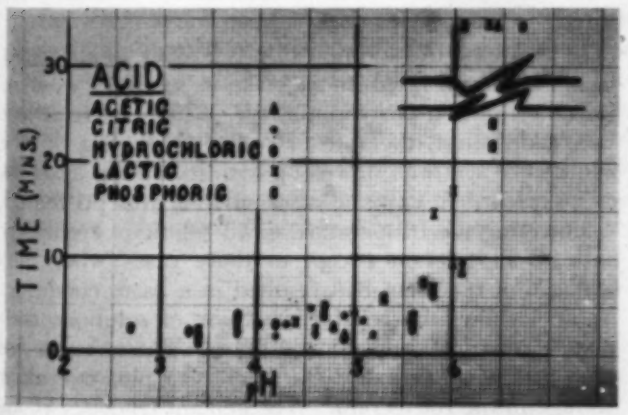


FIG. 1. Relation between pH of solution, acid employed and time required to attain maximum viscosity for 2.00 percent Irish Moss extractive in water.

there was a gradual falling off in viscosity with time. It was also noticed that although the solutions remained clear when the acidity was neutralized, there was an immediate drop in viscosity. Following these observations, viscosity-time curves were determined over a prolonged period for both acidulated and neutralized solutions (Figure 2). A sample of highly purified

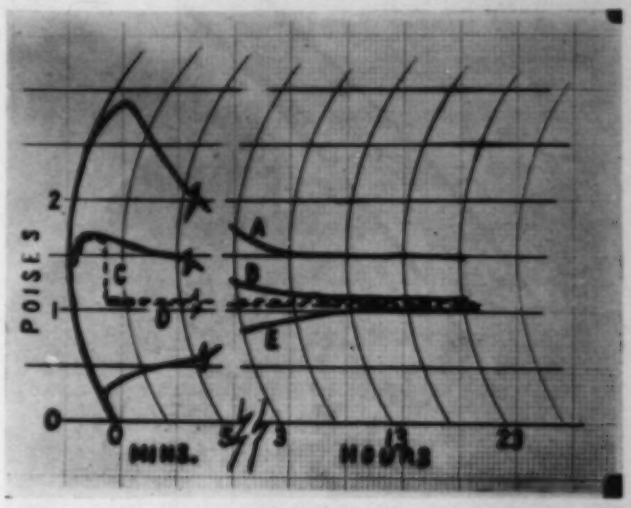


FIG. 2. Viscosity-time relation (Brabender viscosimeter) for 2.00 percent solutions of:
A—highly purified extractive
B—regular extractive in acid solvent
C—same as B, but neutralized after 2 minutes
D—regular extractive dissolved by heat and cooled
E—regular extractive dissolved in deionized water.

extractive was included in this study, since this material exhibits the same rapid solubility typical of acid solutions. For comparison a dispersion of regular extractive in deionized water and a cooled solution of extractive dissolved by heat were included. All solutions were prepared at a concentration of 2.00 percent.

It will be noted that curve A, of the purified hydrocolloid, is similar to curve B, of the regular extractive in acid solution, both rising rapidly to a peak viscosity, then gradually thinning out to a constant consistency within 24 hours. Curve C shows the result when the acid is neutralized. After 2 minutes of acid solution, showing the typical viscosity increase, alkali was added. The viscosity immediately dropped to a constant value identical with that shown in curve D for a solution prepared with heat. Curve E demonstrates that regular extractive in plain water will eventually go into solution. Whether course B, C, D or E is taken, within 24 hours the result is the same.

Evidence for the similarity in the state of the hydrocolloid whether dissolved by heat or with acid is shown by the close similarity of the viscosity-concentration (Figure 3) and the viscosity-temperature curves (Figure 4) for thermal and acid solutions. The empirical relationships plotted for the thermal solutions have been proven out through several years of laboratory and plant use. In both cases the thermal solution curves are for temperature conditions where dissolved salts do not influence the viscosity characteristics. Since the acid solution viscosities, of necessity, were measured

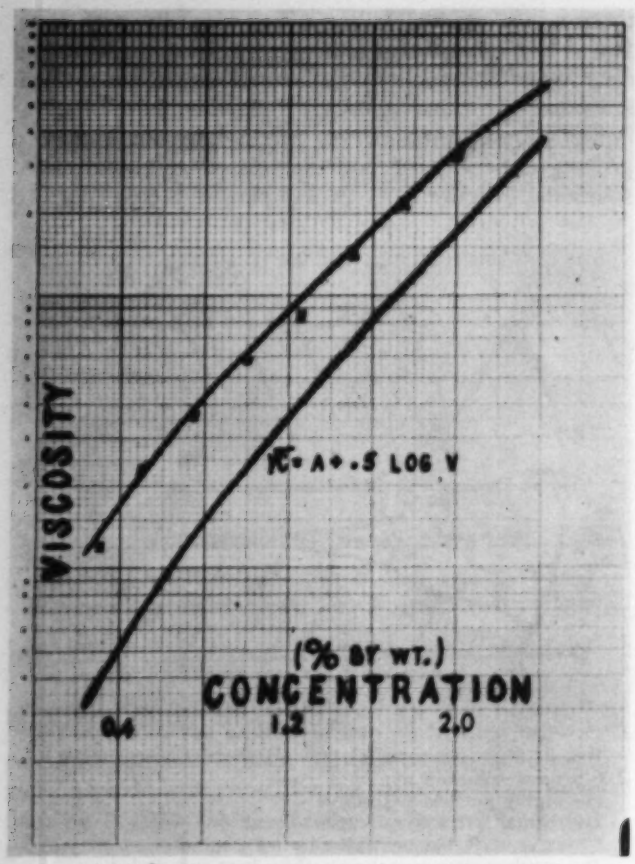


FIG. 3. Viscosity — concentration relation for heated solution ($\sqrt{C} = A + .5 \log V$) and for extractive dissolved by acidulation.

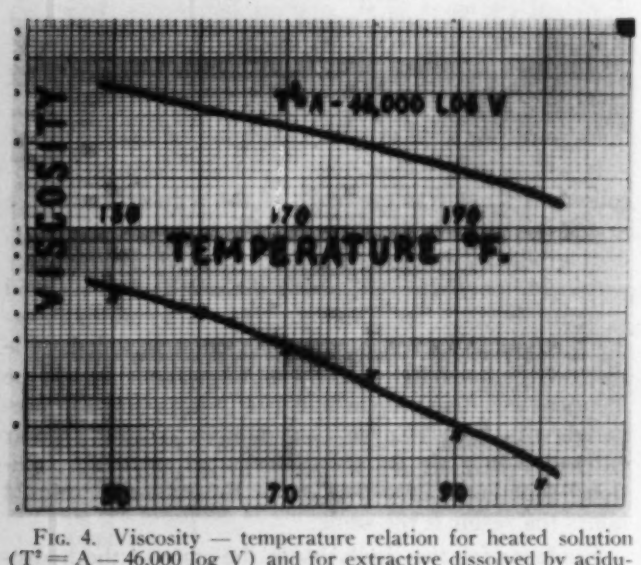


FIG. 4. Viscosity — temperature relation for heated solution ($T^2 = A - 46{,}000 \log V$) and for extractive dissolved by acidulation.

at temperatures where dissolved salts are effective, identical curves could not be expected.

Dissolved materials of many kinds retard the solution of Irish moss extractive and cause the formation of thermally reversible gels when the extractive is finally dissolved by heating. Typical of these, which for convenience we shall call retardents, are potassium chloride, sodium chloride, sucrose and glycerine. Potassium salts in particular are most effective in retarding solution and causing gel formation. The other three are selected because of their common occurrence in food and pharmaceutical preparations.

The influence of retardents on the absorption of water is graphically illustrated when extractive is dispersed in solutions of these materials (Figure 5). The swelled

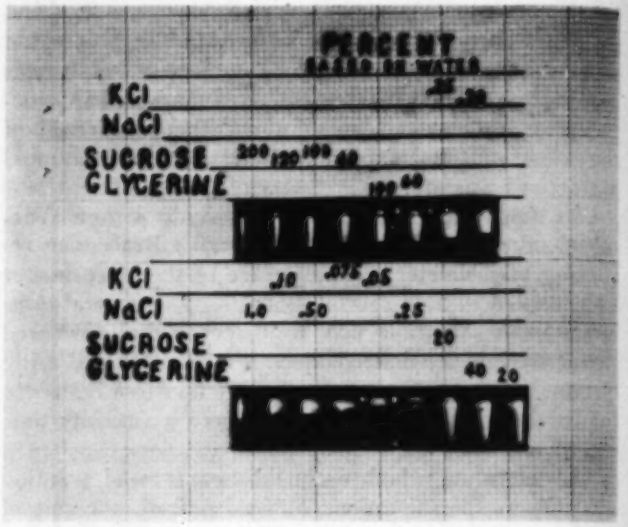


FIG. 5. Influence of retardents at the indicated concentrations on the absorption of water by Irish Moss extractive as shown by the degree of settling on standing. Solutions were at the normal pH of the retardent plus extractive.

particles of hydrocolloid settle, forming a layer in proportion to the amount of water absorbed. In border line cases where there is no settling out of particles, the presence of discreet bodies and lack of clarity give evidence that solution has not been attained. The concentrations of retardents illustrated here are those which were used in studying their influence on acid solutions.

In this study a comparison was made of solutions, prepared by normal heating and cooling with acidulated solutions where retardents were added after acidulation and where retardents were added before the extractive and acid. For ease in dispersion, it was found best to add the extractive to the water, followed by the acid. The effects of neutralization and temperature of storage were also included. The concentration of extractive throughout the series was 2.00 percent of the water.

In all cases, the addition of a retardent to an acidulated solution, caused an increase in viscosity even as far as creating a pasty condition. When the retardent was added first, the rate of water absorption on the addition of acid was slowed up with increasing amounts of retardent. In extreme cases solution was prevented.

Lowering the temperature of all solutions eventually resulted in gelation except in those cases where the addition of retardent had resulted in a pasty condition. Table 1 shows the relative condition of solutions containing retardents added as described. These results are after 2 days storage at 80° F. (27° C.) plus overnight storage in the refrigerator. The general tendency is for increased concentrations of retardent in heated solution to increase both gel strength and gelling temperature.

TABLE 1

*Physical State of Solutions Containing Various Retardents*

Condition of 2.00 percent solutions of Irish moss extractive after 48 hours at 80° F. (27° C.) and an additional 12 hours at 45° F. (7° C.). Indicated retardents were added both after the extractive had been dissolved by acidulation and before the extractive was dispersed in the water.

| | Solutions Prepared By | | | | | |
|---|---|---|---|---|---|---|
| | Heating | | Acidulation | | | |
| Retardent Added: | With Extractive | | After Acidulation | | Before Extractive | |
| (percent based on water) | @ 80° F. | @ 45° F. | @ 80° F. | @ 45° F. | @ 80° F. | @ 45° F. |
| Sucrose | | | | | | |
| 0 | fluid | soft gel | fluid | soft gel | ..... | ..... |
| 20 | fluid | gel | fluid | soft gel | fluid | very soft gel |
| 60 | fluid | gel | pasty | pasty | pasty | soft paste |
| 100 | soft gel | gel | pasty | pasty | slight settling | soft paste |
| 120 | gel | gel | pasty | pasty | settling | settling |
| 200 | gel | gel | pasty | pasty | settling | settling |
| Sodium Chloride | | | | | | |
| 0 | fluid | soft gel | fluid | soft gel | ..... | ..... |
| 0.25 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| 0.50 | fluid | soft gel | pasty | soft gel | pasty | pasty |
| 1.00 | very soft gel | soft gel | pasty | pasty | pasty | pasty |
| Glycerine | | | | | | |
| 0 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| 20 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| 60 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| 100 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| Potassium Chloride | | | | | | |
| 0 | fluid | soft gel | fluid | soft gel | ..... | ..... |
| 0.05 | fluid | soft gel | fluid | soft gel | fluid | soft gel |
| 0.075 | fluid | gel | fluid | soft gel | fluid | soft gel |
| 0.10 | fluid | gel | fluid | soft gel | fluid | soft gel |
| 0.20 | gel | gel | pasty | pasty | settling | pasty |
| 0.25 | gel | gel | pasty | pasty | sharp | settling |

In acid solution increased concentrations of retardents inhibit gel formation. However, after prolonged storage, particularly at high temperature or low pH, the tendency of acidulated solutions is to approach the condition of those prepared by heating. A combination of high storage temperature and low pH should be avoided, as hydrolysis of the extractive will result.

The thickening observed on the addition of retardents is probably an assertion of the gelling reaction, except that the polymer network is not completely formed. Retardents can be added most successfully to an acidulated solution when the solution is first mixed. When hydration is complete, the same difficulty attendant on adding retardents to heated and cooled solutions is encountered. Lumps of gel form around the point of addition of the retardent where the retardent concentration is initially very high.

The effect of retardents is obviously to alter the state of hydration. When this hydration change is started from complete solution, a gel network is formed. When dehydration is started from the state of hydration initially obtained with acid solutions, a random network is probably formed resulting in a pasty condition. Low concentrations of retardents only alter the rate of hydration. At constant temperature higher concentrations result in incomplete hydration. The balance point between hydration and dehydration for any particular retardent concentration is obviously the gelling temperature. To prevent gelation when the temperature drops below the balance point, sufficient retardent must be used to raise that point for all fractions of the extractive above any temperatures that may be encountered in storage.

The mechanism behind the behavior of Irish moss extractive in acid media could be a source of endless speculation. It is evident that the effect of retardents, either occurring naturally or added, in slowing down the rate of water absorption is reduced at low pH. That the low pH influences the hydrocolloid and not the retardent may be concluded from the results with non-ionizable sugar and glycerine.

The Irish moss hydrocolloid is a salt of a sulfuric acid ester of a carbohydrate polymer. This ester is increasingly sensitive to hydrolysis below pH 6. I add these last two items for whatever they may be worth to those who desire to speculate.

This new tool for the utilization of Irish moss extractive shows promise of varied and valuable application. The entire field of emulsions and suspensions in vinegar is already under investigation. This takes in salad dressings, relishes and acid sauces of all types. Flavoring emulsions can now be prepared without the necessity of heating gum solutions. It should be possible to prepare a dry mix to which only water need be added to obtain a baker's type jelly. Individual experience and problems will suggest situations that will be aided by this new solution technique.

# Factors Affecting the Objective and Organoleptic Evaluation of Quality in Raw and Canned Peas[a]

AMIHUD KRAMER, L. E. SCOTT, AND R. B. GUYER
*Department of Horticulture, University of Maryland,*

AND

L. E. IDE
*Production and Marketing Administration, U.S.D.A.*

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**Newly developed objective methods for measuring quality are compared to existing methods and organoleptic evaluations. The effects of varieties, delays in harvesting, holding after shelling, precooling and icing on "T" meters, A. I. S., pigments, ascorbic acid and organoleptic values for tenderness, color, and flavor of raw and canned peas are presented.**

Although the problem of the measurement of quality in peas has received considerable attention from many workers during the last two decades, there is little precise information available pertaining to the consumers' impression of quality in peas. It has been generally recognized that varietal differences, size, maturity (especially as it affects tenderness), color, and flavor, are all factors influencing quality. A labeling survey conducted for the National Canners Association *(16)* indicated that consumer understanding of quality was influenced primarily by size of peas. In a more recent consumer survey, Larsen and Stier *(9)* concluded that consumers considered flavor to be first in importance, followed in order of importance by texture, color, and size.

In attempts to establish objective methods for determining quality of peas, there has been a tendency to search for one rapid procedure which would hold the key to overall quality. Since several factors of quality are associated with maturity, much of the work was concentrated on the development of methods for measuring maturity changes.

For grading of raw peas, Walls *(22)* proposed a method based on salt flotation and size. Jodidi described a method based on specific gravity *(6)*.

The tenderometer, developed by Martin *(12)*, and the texturemeter developed by Christel *(3)* are being used extensively in the industry primarily as indicators of maturity. The relative precision of these instruments and their usefulness in predicting the quality of the canned product have been studied by Walls, et al. *(23, 24)*, and Kramer *(8)*, and their relation to the frozen product, by Lee *(10)* and Nielsen et al. *(13)*. The United States Department of Agriculture standards for fresh shelled peas for canning or freezing are based primarily on organoleptic measurements of tenderness, although in practice, reference is made to tenderometer or texturemeter values as related to grades *(20)*. Temperature summations are in use to determine proper dates of harvest *(17)*. Bonney suggested the use of pod color as an index of quality, but Mahoney *(11)* demonstrated this method to be inferior to other methods.

For the canned product, Kertesz *(7)* recommended the alcohol insoluble solids method, which has since been adopted by the Food and Drug Administration as the official method for determining the standard of quality *(1)*. In addition to the clearness of liquor and absence of defects, the United States Department of Agriculture standards for canned and frozen peas are based largely on maturity as measured by a brine flotation method, and uniformity of color *(21)*. The limitations of the brine flotation method and its relation to the alcohol insoluble solids test have been discussed by Smith and Kramer *(19)*.

Regarding the frozen product, considerable attention has been directed to skin texture *(14)*. Lee *(10)* proposed a specific gravity test. Application of the AIS test is under consideration for the frozen product *(5)*.

It is thus apparent that the objective evaluation of quality, especially of raw peas, is based almost entirely on measurements reflecting maturity which imply that younger peas are always more acceptable than older peas, without regard to factors such as flavor and color, which may or may not be positively correlated with measurements of maturity. The purpose of these investigations therefore, was to evaluate critically the important factors of quality when measured by organoleptic and objective methods, as affected by such practical conditions as delay in harvest, holding after shelling, pre-cooling and icing, and varietal differences.

## Materials and Methods

Strains of Alaska and Thomas Laxton peas were planted in the spring of 1948 at the Plant Research Farm of the University of Maryland. Each variety was harvested at six successive dates. The first harvest was made when the peas were extremely young—somewhat too young for commercial canning. The last harvest was made at a date when the peas were border-line standard—sub-standard in respect to maturity. At each date of harvest, the material was divided into two lots. One was pre-cooled in ice water immediately after vining, placed in lug boxes, and kept covered with crushed ice for the duration of the holding period. The other lot was held at room temperature. Each lot was

[a]Scientific Publication No. A254, Contribution No. 2189, of the Maryland Agricultural Experiment Station (Department of Horticulture). Partial Support from funds provided under the research and Marketing Act of 1946, Project NEM3.

TABLE 1

*Effect of Post-Harvest Handling on Objective Evaluations of Quality of the Raw Shelled Peas.*

| | | Tender-ometer | Texture-meter | A. I. S. | Color | Ascorbic acid |
|---|---|---|---|---|---|---|
| Main effects: | | | | | | |
| 1. Date of Harvest. | | | | | | |
| 1st | | 85 | 80 | 9.6 | 49 | 23 |
| 2nd | | 90 | 86 | 11.5 | 70 | 25 |
| 3rd | | 103 | 96 | 13.2 | 76 | 28 |
| 4th | | 127 | 127 | 17.0 | 100 | 29 |
| 5th | | 158 | 158 | 21.6 | 114 | 29 |
| 6th | | 192 | 190 | 25.9 | 129 | 17 |
| L. S. D.[1] | | 3.1 | 5.2 | 0.31 | 11.2 | 4.0 |
| F value | | 1497.6[d] | 567.1[d] | 3285.9[d] | 56.5[d] | 10.2[c] |
| 2. Holding after vining. | | | | | | |
| 2 hours | | 125 | 125 | 16.6 | 93 | 27 |
| 8 hours | | 126 | 123 | 16.5 | 100 | 25 |
| 24 hours | | 126 | 119 | 16.4 | 77 | 24 |
| L. S. D.[1] | | 2.2 | 3.6 | 0.22 | 7.8 | 2.8 |
| F value | | 0.8– | 5.1[b] | 1.4– | 17.7[c] | 2.9[b] |
| 3. Pre-cooling and Icing. | | | | | | |
| Pre-cooled and iced | | 124 | 122 | 15.6 | 95 | 26 |
| Not pre-cooled and iced | | 128 | 123 | 17.3 | 85 | 25 |
| L. S. D.[1] | | 1.8 | 3.0 | 0.18 | 6.4 | 2.2 |
| F value | | 16.9[c] | 1.5– | 386.4[d] | 9.5[c] | 1.2– |
| 4. Varieties. | | | | | | |
| T. L. | | 120 | 118 | 15.3 | 91 | 23 |
| Alaska | | 132 | 127 | 17.7 | 89 | 28 |
| L. S. D.[1] | | 1.8 | 3.0 | 0.18 | 6.4 | 2.2 |
| F value | | 195.0 | 38.2 | 701.8 | 0.4 | 18.9 |
| Interactions: | | | | | | |
| 1 x 2—Dates of Harvest × holding after vining. | | | | | | |
| Dates | Hours | | | | | |
| 1st | 2 | 85 | 82 | 9.6 | 54 | 24 |
| | 8 | 88 | 84 | 9.5 | 56 | 25 |
| | 24 | 82 | 74 | 9.8 | 37 | 22 |
| 2nd | 2 | 90 | 91 | 11.3 | 67 | 28 |
| | 8 | 90 | 86 | 11.1 | 87 | 25 |
| | 24 | 91 | 80 | 12.0 | 57 | 21 |
| 3rd | 2 | 104 | 99 | 13.3 | 73 | 32 |
| | 8 | 103 | 99 | 12.9 | 90 | 28 |
| | 24 | 102 | 91 | 13.5 | 65 | 24 |
| 4th | 2 | 126 | 128 | 17.0 | 109 | 31 |
| | 8 | 128 | 128 | 17.5 | 114 | 29 |
| | 24 | 127 | 124 | 16.7 | 78 | 28 |
| 5th | 2 | 157 | 159 | 21.9 | 126 | 28 |
| | 8 | 156 | 153 | 22.0 | 117 | 28 |
| | 24 | 162 | 158 | 20.8 | 101 | 31 |
| 6th | 2 | 191 | 192 | 26.3 | 130 | 18 |
| | 8 | 192 | 189 | 25.9 | 133 | 18 |
| | 24 | 193 | 189 | 25.5 | 123 | 16 |
| L. S. D.[1] | | 5.4 | 9.0 | 0.54 | 19.5 | 7.0 |
| F value | | 1.2– | 0.9– | 6.0[b] | 1.1– | 0.7– |
| 1 × 3—Dates of Harvest × pre-cooling and icing. | | | | | | |
| Dates | Cooling | | | | | |
| 1st | Yes | 84 | 80 | 9.0 | 53 | 25 |
| | No | 85 | 79 | 10.2 | 45 | 22 |
| 2nd | Yes | 92 | 86 | 10.5 | 76 | 26 |
| | No | 89 | 85 | 12.4 | 64 | 24 |
| 3rd | Yes | 101 | 98 | 12.5 | 87 | 30 |
| | No | 104 | 94 | 14.0 | 65 | 27 |
| 1 × 3—(Continued) | | | | | | |
| 4th | Yes | 120 | 120 | 15.5 | 104 | 29 |
| | No | 133 | 133 | 18.6 | 97 | 29 |
| 5th | Yes | 153 | 153 | 20.6 | 120 | 28 |
| | No | 163 | 163 | 22.6 | 109 | 29 |
| 6th | Yes | 193 | 192 | 25.4 | 129 | 17 |
| | No | 191 | 188 | 26.3 | 128 | 18 |
| L. S. D.[1] | | 4.8 | 7.4 | 0.44 | 5.0 | 5.6 |
| F value | | 9.7[c] | 3.6[b] | 386.4[d] | 0.8– | 0.5– |
| 1 × 4—Dates of Harvest × varieties. | | | | | | |
| Date | Varieties | | | | | |
| 1st | T. L. | 81 | 74 | 8.6 | 62 | 16 |
| | Al. | 89 | 85 | 10.7 | 37 | 31 |
| 2nd | T. L. | 86 | 79 | 10.4 | 83 | 16 |
| | Al. | 95 | 93 | 12.6 | 57 | 34 |
| 3rd | T. L. | 96 | 92 | 11.2 | 77 | 24 |
| | Al. | 110 | 100 | 15.3 | 75 | 32 |
| 4th | T. L. | 123 | 129 | 16.3 | 117 | 29 |
| | Al. | 130 | 124 | 17.8 | 84 | 29 |
| 5th | T. L. | 155 | 153 | 20.5 | 110 | 34 |
| | Al. | 161 | 161 | 22.6 | 119 | 23 |
| 6th | T. L. | 177 | 180 | 24.8 | 96 | 17 |
| | Al. | 207 | 200 | 26.9 | 161 | 18 |
| L. S. D.[1] | | 4.4 | 7.4 | 0.44 | 15.8 | 5.6 |
| F value | | 14.6[c] | 4.8[b] | 15.7[c] | 21.5[d] | 1 3.7[c] |
| 2 × 3—Hours holding × pre-cooling and icing. | | | | | | |
| Hours | Cooling | | | | | |
| 2 | Yes | 123 | 123 | 16.0 | 93 | 26 |
| | No | 127 | 127 | 17.1 | 94 | 28 |
| 8 | Yes | 124 | 122 | 15.8 | 99 | 24 |
| | No | 128 | 125 | 17.1 | 100 | 26 |
| 24 | Yes | 125 | 120 | 15.0 | 93 | 27 |
| | No | 128 | 118 | 17.8 | 61 | 12 |
| L. S. D.[1] | | 3.1 | 5.2 | 0.18 | 11.2 | 4.0 |
| F value | | 0.3– | 1.9– | 102.6[c] | 12.9[c] | 6.2[c] |
| 2 × 4—Hours holding × varieties. | | | | | | |
| Hours | Variety | | | | | |
| 2 | T. L. | 119 | 121 | 15.4 | 97 | 24 |
| | Al. | 131 | 129 | 17.7 | 89 | 30 |
| 8 | T. L. | 120 | 118 | 15.2 | 98 | 23 |
| | Al. | 132 | 128 | 17.8 | 101 | 28 |
| 24 | T. L. | 120 | 114 | 15.3 | 77 | 22 |
| | Al. | 132 | 124 | 17.8 | 76 | 25 |
| L. S. D.[1] | | 3.2 | 5.2 | 0.18 | 11.2 | 4.0 |
| F value | | 0.1– | 0.2– | 2.5– | 1.1– | 1.1– |
| 3 × 4—Pre-cooling and icing × varieties. | | | | | | |
| Cooling | Variety | | | | | |
| Yes | T. L. | 118 | 117 | 14.3 | 95 | 23 |
| | Al. | 130 | 126 | 16.9 | 95 | 28 |
| No | T. L. | 121 | 119 | 16.3 | 87 | 22 |
| | Al. | 134 | 128 | 18.4 | 83 | 27 |
| L. S. D.[1] | | 2.5 | 4.2 | .26 | 9.2 | 3.2 |
| F value | | 0.1– | 0.1– | 5.7 | .3– | 0.0– |

[b] Significant at the 5% level. [c] Significant at the 1% level. [d] Important differences. – Not significant. [1] Least significant difference.

TABLE 2

*Effect of Post-Harvest Handling on Objective and Organoleptic Evaluations of Quality of Canned Peas.*

| | Objective | | Organoleptic | | |
|---|---|---|---|---|---|
| | A. I. S. | Color | Tenderness | Color | Flavor |
| **Main Order Effects** | | | | | |
| 1. Date of Harvest. | | | | | |
| 1st | 10.0 | 87 | 7.8 | 6.6 | 5.6 |
| 2nd | 11.2 | 88 | 7.6 | 6.8 | 5.7 |
| 3rd | 13.0 | 92 | 6.7 | 7.0 | 5.5 |
| 4th | 15.7 | 107 | 6.7 | 7.2 | 6.1 |
| 5th | 19.1 | 95 | 5.5 | 7.2 | 4.8 |
| 6th | 21.4 | 84 | 4.0 | 6.2 | 4.3 |
| L. S. D.[1] | 0.82 | 5.6 | 0.25 | 0.47 | .80 |
| F value | 499.4‡ | 18.0‡ | 256.1‡ | 5.2† | 5.5† |
| 2. Holding after vining. | | | | | |
| 2 hours | 15.0 | 96 | 6.7 | 6.9 | 6.4 |
| 8 hours | 15.3 | 95 | 6.4 | 6.9 | 5.7 |
| 24 hours | 14.9 | 86 | 6.0 | 6.7 | 3.8 |
| L. S. D.[1] | 0.40 | 4.0 | 0.18 | 0.33 | 0.56 |
| F value | 2.06– | 13.9‡ | 36.6‡ | 0.60– | 47.9‡ |
| 3. Pre-cooling and icing. | | | | | |
| Pre-cooled and iced. | 14.7 | 93 | 6.6 | 6.7 | 5.9 |
| Not pre-cooled and iced | 15.4 | 92 | 6.2 | 6.9 | 4.8 |
| L. S. D.[1] | 0.33 | 3.2 | 0.16 | 0.27 | .46 |
| F value | 15.91‡ | 0.5– | 32.6‡ | 3.2* | 22.2‡ |
| 4. Varieties. | | | | | |
| Thomas Laxton | 13.9 | 91 | 6.7 | 7.3 | 5.4 |
| Alaska | 16.3 | 94 | 6.1 | 6.3 | 5.2 |
| L. S. D.[1] | 0.33 | 3.2 | 0.16 | 0.27 | .46 |
| F value | 208.07‡ | 2.97– | 76.9‡ | 49.9‡ | 1.21– |
| **Interactions.** | | | | | |
| 1 × 2—Dates of harvest × holding after vining. | | | | | |
| Dates Hours | | | | | |
| 1st 2 | 9.7 | 89 | 8.2 | 6.8 | 6.9 |
| 8 | 10.3 | 90 | 7.9 | 6.3 | 6.4 |
| 24 | 9.9 | 84 | 7.3 | 6.7 | 3.5 |
| 2nd 2 | 11.4 | 89 | 8.2 | 6.8 | 6.9 |
| 8 | 11.4 | 91 | 7.7 | 7.1 | 6.8 |
| 24 | 10.9 | 84 | 6.7 | 6.7 | 3.3 |
| 3rd 2 | 13.1 | 92 | 7.0 | 7.0 | 6.5 |
| 8 | 13.3 | 93 | 6.8 | 7.1 | 5.6 |
| 24 | 12.6 | 92 | 6.3 | 6.8 | 4.1 |
| 4th 2 | 16.2 | 112 | 7.1 | 7.2 | 7.5 |
| 8 | 15.5 | 117 | 6.8 | 7.4 | 5.9 |
| 24 | 15.5 | 94 | 6.2 | 6.9 | 4.8 |
| 5th 2 | 18.6 | 105 | 5.8 | 7.3 | 6.1 |
| 8 | 19.7 | 92 | 5.4 | 7.2 | 5.1 |
| 24 | 19.0 | 88 | 5.4 | 7.0 | 3.2 |
| 6th 2 | 20.8 | 88 | 4.0 | 6.1 | 4.7 |
| 8 | 21.6 | 86 | 4.1 | 6.2 | 4.5 |
| 24 | 21.8 | 77 | 3.8 | 6.2 | 3.7 |
| L. S. D[1]. | 1.00 | 9.8 | 0.46 | 0.81 | 1.38 |
| F value | 1.37– | 1.96– | 2.5* | 0.4– | 1.54– |
| 1 × 3—Dates of Harvest × pre-cooling and icing. | | | | | |
| Date Cooling | | | | | |
| 1st Yes | 9.8 | 87 | 8.1 | 6.3 | 5.9 |
| No | 10.1 | 88 | 7.5 | 7.0 | 5.3 |
| 2nd Yes | 10.5 | 88 | 7.9 | 6.7 | 6.4 |
| No | 11.9 | 88 | 7.2 | 7.0 | 5.0 |
| 3rd Yes | 13.0 | 92 | 7.1 | 6.9 | 6.5 |
| No | 13.0 | 92 | 6.4 | 7.1 | 4.4 |
| 1 × 3—(Con.) | | | | | |
| 4th Yes | 15.0 | 106 | 6.9 | 7.0 | 6.8 |
| No | 16.5 | 109 | 6.6 | 7.3 | 5.4 |
| 5th Yes | 18.7 | 100 | 5.8 | 7.1 | 5.3 |
| No | 19.5 | 90 | 5.2 | 7.3 | 4.3 |
| 6th Yes | 21.4 | 84 | 3.8 | 6.3 | 4.3 |
| No | 21.4 | 83 | 4.2 | 6.1 | 4.3 |
| L. S. D.[1] | 0.82 | 8.0 | 0.36 | 0.66 | 1.12 |
| F value | 2.81* | 1.50– | 6.5† | 9.80– | 1.70– |
| 1 × 4—Dates of Harvest × varieties. | | | | | |
| Date Variety | | | | | |
| 1st T. L. | 8.5 | 97 | 8.0 | 7.6 | 5.8 |
| Al. | 11.4 | 77 | 7.5 | 5.7 | 5.5 |
| 2nd T. L. | 10.0 | 95 | 7.6 | 7.5 | 6.1 |
| Al. | 12.4 | 83 | 7.3 | 6.2 | 5.3 |
| 3rd T. L. | 11.6 | 92 | 7.4 | 7.6 | 5.5 |
| Al. | 14.4 | 91 | 6.1 | 6.3 | 5.4 |
| 4th T. L. | 15.0 | 109 | 7.2 | 7.8 | 6.2 |
| Al. | 16.4 | 106 | 6.2 | 6.5 | 6.0 |
| 5th T. L. | 18.2 | 91 | 5.7 | 7.3 | 5.0 |
| A.l | 20.1 | 98 | 5.4 | 7.1 | 4.6 |
| 6th T. L. | 19.9 | 63 | 4.0 | 6.0 | 4.2 |
| Al. | 22.9 | 104 | 3.9 | 6.3 | 4.4 |
| L. S. D.[1] | 0.82 | 8.0 | .36 | 0.66 | 1.12 |
| F value | 2.49 | 27.4 | 6.0 | 6.2 | .36 |
| 2 × 3—Hours holding × pre-cooling and icing. | | | | | |
| Hours Cooling | | | | | |
| 2 Yes | 14.7 | 96 | 6.9 | 6.6 | 6.5 |
| No | 15.3 | 95 | 6.6 | 7.1 | 6.4 |
| 8 Yes | 15.0 | 93 | 6.6 | 6.8 | 5.9 |
| No | 15.6 | 97 | 6.3 | 7.0 | 5.6 |
| 24 Yes | 14.5 | 89 | 6.3 | 6.7 | 5.2 |
| No | 15.3 | 83 | 5.8 | 6.7 | 2.3 |
| L. S. D.[1] | 0.57 | 5.6 | 0.25 | 0.47 | 8.80 |
| F value | 0.14– | 3.54† | 1.75– | 0.9– | 15.7‡ |
| 2 × 4—Hours holding × varieties. | | | | | |
| Hours Variety | | | | | |
| 2 T. L. | 13.9 | 97 | 7.0 | 7.7 | 6.7 |
| Al. | 16.0 | 95 | 6.4 | 6.1 | 6.2 |
| 8 T. L. | 14.3 | 93 | 6.8 | 7.7 | 5.9 |
| Al. | 16.3 | 96 | 6.1 | 6.1 | 5.5 |
| 24 T. L. | 13.5 | 82 | 6.3 | 6.5 | 3.7 |
| Al. | 16.4 | 90 | 5.6 | 6.9 | 3.8 |
| L. S. D.[1] | 0.57 | 5.6 | 0.25 | 0.47 | 0.80 |
| F value | 2.81* | 2.97† | 0.1– | 25.7‡ | .63– |
| 3 × 4—Pre-cooling and icing × varieties. | | | | | |
| Cooled Variety | | | | | |
| Yes T. L. | 13.5 | 92 | 6.8 | 7.4 | 6.0 |
| Al. | 14.3 | 90 | 6.3 | 6.1 | 5.7 |
| No T. L. | 16.0 | 94 | 6.6 | 7.3 | 4.9 |
| Al. | 16.5 | 93 | 5.8 | 6.6 | 4.7 |
| L. S. D.[1] | 0.47 | 10 | 0.20 | 0.38 | 0.66 |
| F value | 0.67– | 0.42– | 2.70* | 6.3† | 0.2– |

* Significant at the 5% level. † Significant at the 1% level. ‡ Important differences. – Not significant. [1] Least significant difference.

then sampled and canned two hours, eight hours, and twenty-four hours after vining.

The following determinations were made on the raw product: tenderometer, texturemeter, alcohol insoluble solids, green pigment, and ascorbic acid. Official P. M. A. grades were provided by a USDA inspector. The remaining material was canned and alcohol insoluble solids and green pigment determinations were made on the canned product. Organoleptic determinations for tenderness, color and flavor were provided by a panel of judges consisting of members of the Departments of Horticulture and Agricultural Economics of the University of Maryland, and the Production and Marketing Administration of the United States Department of Agriculture. The organoleptic determinations were made as follows: for tenderness, 1 was equivalent to sub-standard, up to 8 for optimum tenderness, while 9 and 10 indicated peas that were entirely too immature; for color, 10 indicated the best deep green color while the palest, lightest grey-green samples were graded 1; similarly for flavor, 10 indicated the best flavor while 1 was entirely unacceptable.

Of the objective methods, only the color method has not been reported heretofore. The sample of peas was blended with an equal weight of water in a Waring Blendor, to a uniform pulp. Twenty grams were weighed and transferred to a cup of a Waring Blendor with about 70 ml. acetone and blended for exactly five minutes. The contents were transferred to a graduated 100 ml. cylinder, made up to volume, stirred thoroughly and a suitable portion transferred to a centrifuge tube and centrifuged until clear. The clarified pigment extract was measured in a spectrophotometer or photoelectric colorimeter at a wave length centered about 665 mμ. The color instrument was standardized with a known solution of chlorophyll A and B and calculated as p.p.m. chlorophyll.

## Discussion of Results

The factors of quality to be discussed are tenderness or succulence, color, and flavor. Since the factor of size is intimately associated with texture and is reflected in maturity measurements, the above factors cover all the important aspects of quality of interest to the consumer other than factors of workmanship such as absence of defects.

The data are summarized in Table 1 for the raw peas, and in Table 2 for the canned product. The correlations between the objective and organoleptic tests of quality are presented in Table 3.

*Tenderness.* The tenderometer and the texturemeter are primarily measurements of hardness. Their correlations with alcohol insoluble solids on raw as well as canned peas are so high that it may be concluded that all these tests measure the same quality factor (Table 3). The correlations between the tenderometer or A.I.S. test and the organoleptic test for tenderness of canned peas of .90 is about as high as can be expected and is entirely satisfactory. The lower correlation of .83 between the texturemeter and the organoleptic test is probably due to the lesser degree of precision of the latter instrument. This is borne out by the results of Walls et al. *(23)* who reported a coefficient of variability of 1.56 percent for the tenderometer as compared to 7.5 percent for the texturemeter. The texturemeter, on the other hand, is definitely superior to the tenderometer in several respects. It is light, and may be used in the field; it is less expensive; and what is perhaps most important, it may be standardized by the use of ordinary standard gages.

Although there is a satisfactory chemical method for standardizing tenderometers *(8)*, there is no easy way to accomplish this;[b] consequently, work was initiated to develop a miniature tenderometer which would combine the advantages of lightness, inexpensiveness, and ease of standardization with a greater degree of precision. In preliminary work with a newly designed instrument (Figure 1), similar in size to the texturemeter but resembling the tenderometer in the shearing force principle, the average coefficient of variability for this instrument was 3.33 as compared to 1.61 for the tenderometer, and 5.67 for the texturemeter on the same series of samples.

The correlation of .95 between the tenderometer values and A. I. S. values on raw peas would be even higher if it were not for the effect of the pre-cooling and icing treatments. As illustrated in Figure 2, pre-cooled and iced peas tend to grade about eight points higher on the tenderometer than would be predicted from previously prepared tenderometer—A. I. S. prediction charts *(8)*, while tenderometer readings for peas held for as long as 24 hours without cooling, whose flavor is

[b] A method for comparing tenderometers by using peas preserved in alcohol has been recommended by the National Canners Association.

TABLE 3

*Correlations between Objective and Organoleptic Evaluations of Quality Factors of Raw and Canned Peas.*

| | Objective tests | | | | | | | Organoleptic tests on canned peas | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | On raw peas | | | | | On canned peas | | | | |
| | Tenderometer | Texturemeter | A. I. S. | Pigment | Ascorbic Acid | A. I. S. | Pigment | Tenderness | Color | Flavor |
| Tenderometer | .... | .97 | .95 | .62 | .02 | .97 | .14 | .90 | .14 | .36 |
| Texturemeter | .97 | .... | .89 | .66 | .03 | .96 | .21 | .83 | .16 | .24 |
| Raw A. I. S. | .95 | .89 | .... | .62 | .14 | .96 | .12 | .90 | .21 | .43 |
| Raw Pigment | .62 | .66 | .62 | .... | .06 | .62 | .57 | .11 | .61 | .01 |
| Raw Ascorbic Acid | .02 | .03 | .14 | .06 | .... | .07 | .43 | .13 | .16 | .29 |
| Canned A. I. S. | .97 | .96 | .96 | .62 | .07 | .... | .17 | .89 | .16 | .34 |
| Canned Pigment | .14 | .21 | .12 | .57 | .43 | .17 | .... | .05 | .50 | .44 |
| Organ. Tenderness | .90 | .83 | .90 | .11 | .13 | .89 | .05 | .... | .20 | .59 |
| Organ. Color | .14 | .16 | .21 | .61 | .16 | .16 | .50 | .20 | .... | .17 |
| Organ. Flavor | .36 | .24 | .43 | .01 | .29 | .34 | .44 | .59 | .17 | .... |

.23—significant at the 5% level. .30—significant at the 1% level. Multiple correlation of flavor x A. I. S., Pigment, Ascorbic Acid—.58.

FIG. 1. The miniature tenderometer.

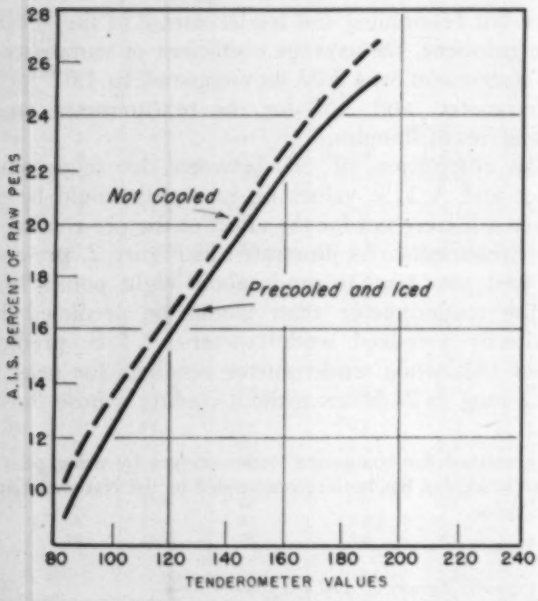


FIG. 2. Effect of precooling and icing on relation of tenderometer values to A. I. S. % of raw peas.

very poor, show very precise agreement with predicted values. This differential effect of water cooling is not retained in the relation of tenderometer readings to A.I.S. of the canned product (Figure 3), thus indicating that water cooling has a permanent though slight effect of hardening the peas so treated. From the practical standpoint it is extremely important to note that the tenderometer and other instruments for measuring tenderness do not in the least reflect gross deterioration

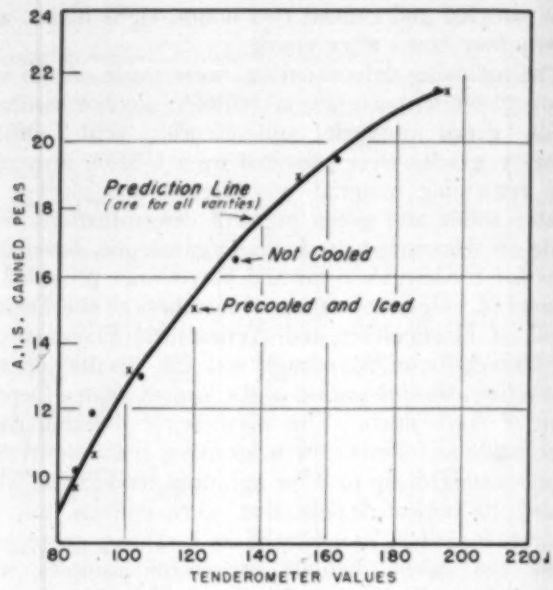


FIG. 3. Effect of precooling and icing on the relation of tenderomter values on raw peas to A. I. S. % on canned peas.

in quality resulting from holding peas after shelling without cooling.

The relation of tenderometer values to A. I. S. values on canned peas is definitely affected by varieties, as indicated in Figure 4, where the same tenderometer

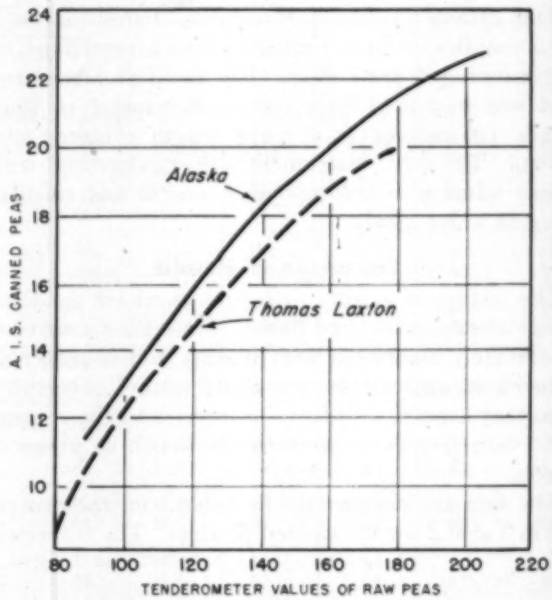


FIG. 4. Effect of varieties on relation of tenderometer values on raw peas to A. I. S. % of canned peas.

values indicate higher A. I. S. results for Alaska than for Thomas Laxton peas.

The data in Table 1 further substantiate the fact that date of harvest of a given planting is of primary importance in determining tenderness as measured organoleptically, or objectively by tenderometer, texturemeter, or A. I. S. on the raw or canned product. Holding shelled peas for as long as 24 hours, whether pre-cooled or not, has relatively little effect on this factor of tenderness.

*Color.* The color factor, though mentioned in standards of quality, and accepted as a factor of quality, has not previously been measured by objective methods. The method herein described provided the opportunity for many interesting observations. In general, organoleptic values for color varied much less than similar values for tenderness and flavor (Table 2). Thus whereas values for tenderness as affected by date of harvest varied from 7.8 to 4.0, values for color varied only from 7.2 to 6.2. Similarly where the values for flavor as affected by holding after shelling varied from 6.4 to 3.8, those for color varied only from 6.9 to 6.7. The color factor on the other hand was affected by varietal difference to a greater extent than either tenderness or flavor. This varietal effect is illustrated in Figure 5, which shows that organoleptically, Alaska

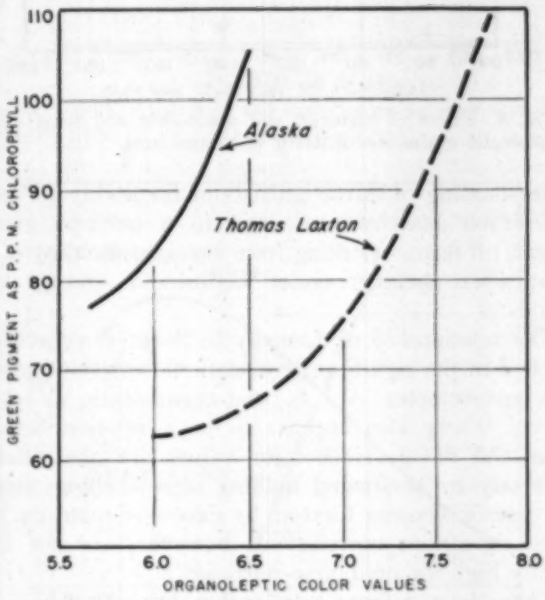


FIG. 5. Effect of varieties on relation of green pigment values to organoleptic evaluation of color.

peas vary from 5.7 to 6.5, while Laxton Peas having a similar range of green pigment content vary from 7.0 to 7.8 organoleptically.

This small range organoleptically, combined with the relatively tremendous varietal difference tends to reduce the correlation between the raw pigment content and organoleptic evaluation of color to .61 which though highly significant, is not sufficiently high for predictive purposes. Another factor which may reduce the value of this correlation is that holding of peas after shelling reduces the green pigment content but at the same time appears to favor the development of a brownish color which upon canning may pass for deeper green.

The correlation between raw pigment content and canned pigment content of .57 is also surprisingly low. Again this is partly explained by the difference in varietal behavior, as illustrated in Figure 6. Apparently Alaska peas continue to increase in pigment content with increasing maturity, while Thomas Laxton peas increase in pigment content to a point where the tenderometer value is about 125. Beyond this point, there is a tendency to lose pigment.

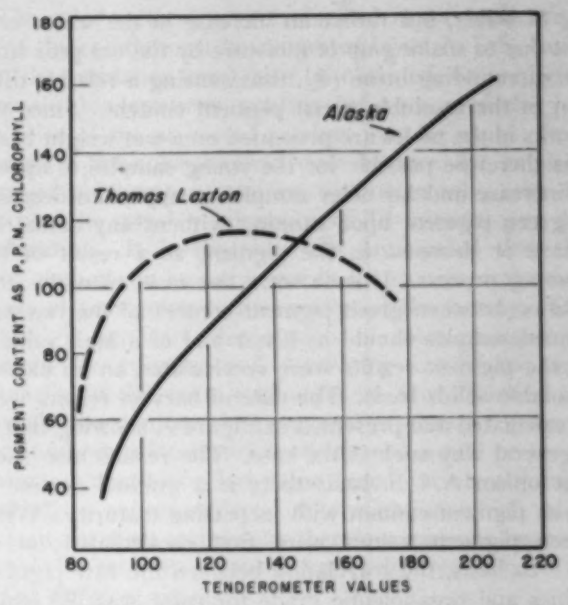


FIG. 6. Effect of varieties on the relation of green pigment content to maturity as measured by tenderometer values.

When comparing the raw and canned pigment values in Tables 1 and 2, and Figure 7, it appears that as related to the raw pigment values, the young canned samples show a considerable loss in green pigment. An explanation for this peculiar relationship may be based on the chemical composition of peas at different stages

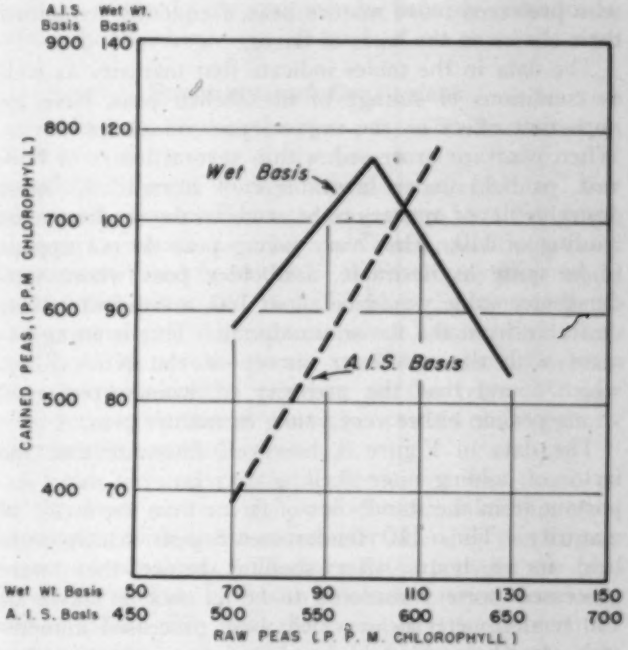


FIG. 7. Relation of pigment content of raw peas to canned peas as expressed on a wet weight basis, and A. I. S. basis.

of maturity. Very young peas contain relatively high sugar and low starch content. Upon canning, much of the soluble sugars is leached out of the peas, thus relatively increasing the insoluble pigment content. With old samples, the reverse may be true. Old peas contain little soluble sugars, but large amount of insoluble starches. Upon canning, there occurs very little leach-

ing of solids, but rather an increase in the water content due to soaking up of moisture by the old peas from the surrounding brine *(8)*, thus causing a relative dilution in the insoluble green pigment content. Since the results in the tables are presented on a wet weight basis, it is therefore possible for the young samples to appear to increase and for older samples to appear to decrease in green pigment upon canning without any actual increase or decrease in the pigment as a result of the canning process. If such were the case, then the correlation between green pigment content of the raw and canned samples should be linear and of a high value if all the pigment results were recalculated on an alcohol insoluble solids basis. The date of harvest results were so calculated and presented in Figure 7, showing that in a general way such is the case. The results also show that on an A. I. S. basis there is a gradual decline in green pigment content with increasing maturity. When green pigment values were first recalculated on an A. I. S. basis, the correlation between the raw pigment values and organoleptic grade for color was .88 which is a satisfactory correlation for prediction purposes.

*Flavor.* The flavor of peas as well as that of many other commodities, is very difficult to define. In fact, an opinion exists that flavor by definition is not a concrete characteristic that is capable of objective evaluation, since it is entirely subjective and thus may mean different things to different consumers *(18)*. It is interesting to note that Larsen and Stier *(9)* found that consumers who preferred very young peas, as well as those who preferred more mature peas, frequently explained their choice on the basis of flavor.

The data in the tables indicate that maturity as well as conditions of storage of the shelled peas, have an important effect on the organoleptic values for flavor. When peas are processed within several hours of harvest, or held under favorable cool storage, the most desirable flavor appears to be at about the tenderometer reading of 110. Thus very young peas do not appear to be quite as desirable, and older peas whose tenderometer value would be about 160, are definitely less desirable from the flavor standpoint. This is in agreement with the consumer survey of the NCA *(16)*, which found that the majority of women preferred young peas to either very young or mature peas.

The data in Figure 8, however, illustrate that the factor of holding after shelling may be even more important from the standpoint of flavor than the factor of maturity. Thus 110 tenderometer peas which were held for 8 hours after shelling before they were processed, were considered to be as poor in flavor as 150 tenderometer peas which were processed immediately after harvest. Additional evidence, indicating that holding after harvest without proper cooling is even more detrimental to flavor than maturity, is presented in Figure 8, where peas which were held for 24 hours without cooling dropped from a flavor value of 6.4 to 2.3, while similar peas which were pre-cooled and iced dropped only to a value of 5.2. Samples which were definitely sub-standard because of advanced maturity, on the other hand, were not lower than 4.2 in their flavor score. It may thus be concluded that organoleptic

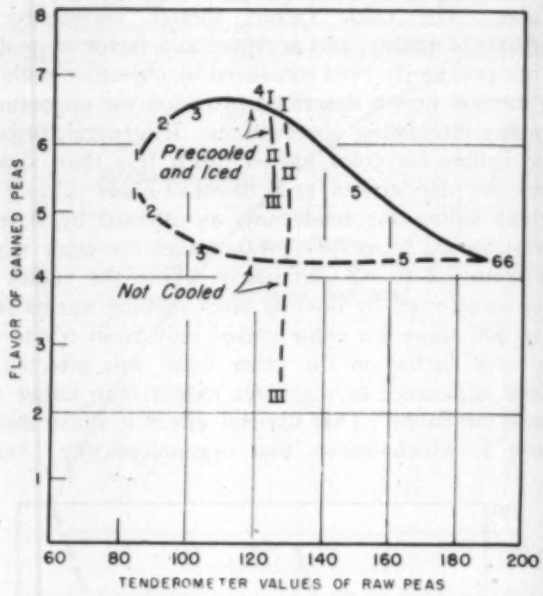


FIG. 8. Effect of maturity and precooling and icing on the organoleptic evaluation of flavor of canned peas.

understanding of flavor consists of the ability to detect undesirable starchy peas, and to a perhaps greater extent, off flavor resulting from excessive holding of the peas, after shelling, under undesirable storage conditions.

The relationship of maturity to flavor is reflected in Table 3 in the significant correlations between maturity and tenderometer, A. I. S., and organoleptic values for flavor. There also appears to be a relation between color and flavor, since color values are also affected adversely by prolonged holding after shelling, and in the case of Thomas Laxton, by excessive maturity. All these significant correlations, however, are not sufficiently high for predictive purposes.

There is a definite relationship between flavor and ascorbic acid. The very low correlation of .29 is due primarily to the entirely different behavior of ascorbic acid in the two varieties studied. With the exception of the extremely young samples, ascorbic acid content in Alaska peas is reduced with increasing maturity. With Thomas Laxton exactly the reverse is true. Ascorbic acid content increases until a value of about 150 tenderometer is reached. Beyond this point, ascorbic acid content of Thomas Laxton peas also goes down rapidly (Figure 9). Thus when ascorbic acid of Alaska samples only was compared with organoleptic values for flavor, the correlation of .74 was obtained. The relation of ascorbic acid to color is also affected tremendously by varietal differences. The data in Figure 10 show that there is a negative correlation for Alaska peas, but a positive correlation for Thomas Laxton peas.

Since significant correlations exist between flavor and the three objective measurements of A. I. S., pigment content, and ascorbic acid, it was thought that perhaps a multiple correlation involving all three determinations would result in a sufficiently high correlation. Such a correlation, however, was calculated as .58, which though better than any individual correlation, was still not sufficiently high for predictive purposes.

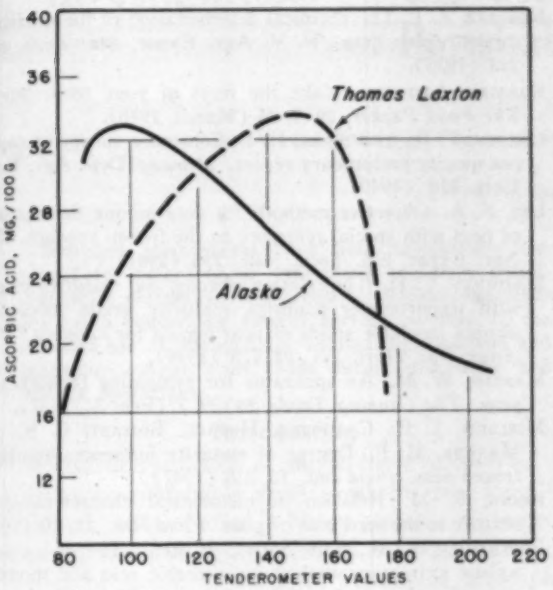


FIG. 9. Effect of maturity and varieties on ascorbic acid content of raw peas.

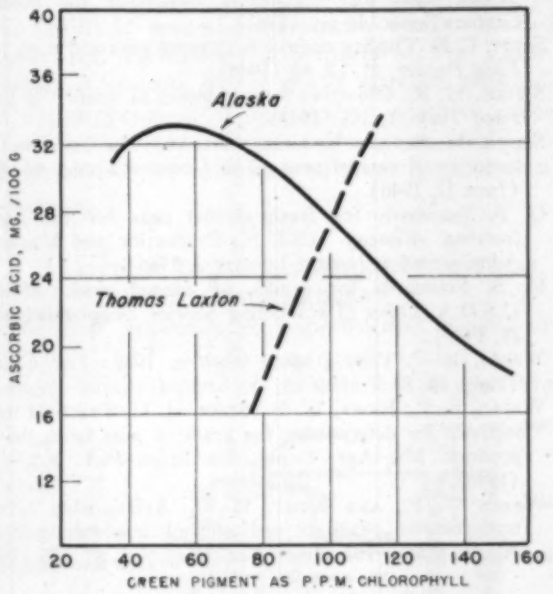


FIG. 10. Effect of varieties on the relation between ascorbic acid and green pigment content of raw peas.

A similar multiple correlation based on samples of the Alaska variety only, yielded a value of .97. It appears possible, therefore, that a multiple regression formula based on tenderometer, ascorbic acid, and pigment values would predict with satisfactory accuracy the organoleptic value for flavor of canned Alaska peas.

## Some Practical Considerations

Instruments like the tenderometer and texturemeter are of immediate and direct practical value. A test may be accomplished in a matter of a minute by any person who is not necessarily highly skilled as a technician. The results predict with a high degree of accuracy the hardness of the raw, canned or frozen material as measured organoleptically, or as indicated by the A. I. S. method.

The color method is more limited in its application. Since the results must be converted to an A. I. S. basis, that determination must also be obtained, or predicted from the tenderometer reading before a prediction of the color of the processed product may be made. Furthermore, the color method does require the employment of a laboratory trained technician who may be expected to spend a minimum of 10 minutes per determination. It is therefore not anticipated that the color method can be put to use in the routine evaluation of lots of peas going to the market or the factory. The method is applicable for studies of color changes, as affected by growing and marketing conditions, and primarily in the color evaluation of new varieties. It may also be used on the processed product by government and other interested agencies who would prefer to obtain an absolute color value based on an objective method, to an organoleptic determination which is of necessity relative and results therefore may not be comparable for samples examined under different conditions and at different times.

There is as yet no method for determining the flavor of raw or canned peas. The extremely high correlation between flavor, and tenderometer, pigment content, and ascorbic acid combined, indicates that it may be possible to determine objectively the flavor of a specific variety of peas. Such a determination, however, would require at least one hour per sample, and the services of a trained technician. It is applicable only to the raw product, since ascorbic acid, a component of the formula, is affected very seriously by canning procedures, especially blanching.

## Summary and Conclusions

Alaska and Thomas Laxton peas were harvested at successive dates over the entire canning range, subjected to different storage conditions after vining, and processed. Tenderometer, texturemeter, A. I. S., green pigment content, ascorbic acid determinations, and inspections based upon the U. S. Standards were made on the raw peas; and A. I. S. green pigment content, and organoleptic determinations for tenderness, color, and flavor were made on the canned product. Correlations were calculated between all the tests. A new miniature tenderometer was also studied and preliminary results reported.

Of the "T"-meters, the tenderometer was found to be the most precise, followed by the miniature tenderometer, with the texturemeter showing the largest degree of variability. The correlation between the tenderometer and A. I. S. both raw and canned, was very high (.95 and .97), and the correlation between either tenderometer or A. I. S. and organoleptic tenderness was satisfactory (.90). Pre-cooling in ice water and icing caused tenderometer readings to average 8 pounds higher than similar material not so treated, but prevented the development of a definite off-flavor noted in the untreated material. Tenderometer and similar measurements were affected primarily by date of harvest, and to a lesser extent by varieties. Holding shelled peas without water cooling had no effect whatsoever on these measurements.

Green pigment determinations of the raw peas were closely correlated with green pigment and organoleptic color determinations of canned peas only after the green pigment values were recalculated on an A. I. S. basis. Green pigment content of Alaska peas increased consistently with maturity while with Thomas Laxton peas there was a reduction in the pigment content at the nearly mature stage.

Flavor of canned peas appeared to consist of the factors of maturity and holding after shelling, of which the latter was decidedly more important. Only peas approaching the sub-standard level of maturity had a detrimental effect on flavor evaluation; on the other hand, there developed an off-flavor which was easily detected after eight hours holding at room temperature and which became highly offensive upon longer periods of holding without cooling. Ascorbic acid determinations showed the best correlation with flavor, but only when individual varieties were considered separately. For example, Alaska peas contained less ascorbic acid as they matured, while Thomas Laxton peas increased in ascorbic acid until a tenderometer reading of about 160. A multiple correlation consisting of tenderometer, pigment, and ascorbic acid, and flavor when based on Alaska values only was satisfactory, but is too involved for routine use as an objective test for flavor.

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# Investigations on the Use of Nitrogen for the Stabilization of Perishable Food Products[a]

A. L. BAYES

*Laboratory of The Linde Air Products Company, Tonawanda, N. Y.*

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**Nitrogen atmospheres have been successfully employed for retarding or preventing oxidative deterioration of perishable food products. Recommendations are given concerning several factors involved in the effective use of nitrogen for eliminating dissolved and headspace oxygen from foods during processing and storage operations.**

## Introduction

The destructive action of atmospheric oxygen on various types of perishable food products has long been recognized and studied. Many types of improved processing and packaging methods have been developed to avoid or minimize harmful effects of atmospheric exposure, but the ultimate benefits of such methods usually depend upon the effectiveness of oxygen removal and exclusion during normal shelf-life storage. The results of several experimental studies carried on in the Food Technology Laboratory of The Linde Air Products Company on the use of nitrogen atmospheres for the suppression of destructive oxidative processes are discussed here. Other experiments dealing with the prevention or inhibition of food deterioration are continuing.

## PART I

### Analytical Techniques Employed in These Investigations

The first approach to experimental phases of the problem, based on the assumption that protective methods would depend on the extent of oxygen removal and exclusion, was the development of suitable techniques for the accurate analysis of dissolved and headspace gases.[b] Essential features are shown in Figure 1. The sample is introduced at point (C), and gas desorption is achieved by recycling liquid between chambers (A) and (B) through the spray jet (D). Pressure and vacuum on the system, as required, are obtained by means of adjusting mercury reservoir (E). Desorbed gases collected in (B) are removed and analyzed by standard Orsat procedures in buret (F), to give compositions in terms of carbon dioxide, oxygen, and nitrogen (by difference). The apparatus was made portable and gave satisfactory service in both laboratory and field tests. Accuracy of the method, determined by oxygen analysis in distilled water samples saturated with air at various temperatures, showed an average deviation of approximately one percent. Such accuracy is considered adequate for analytical control of food processes.

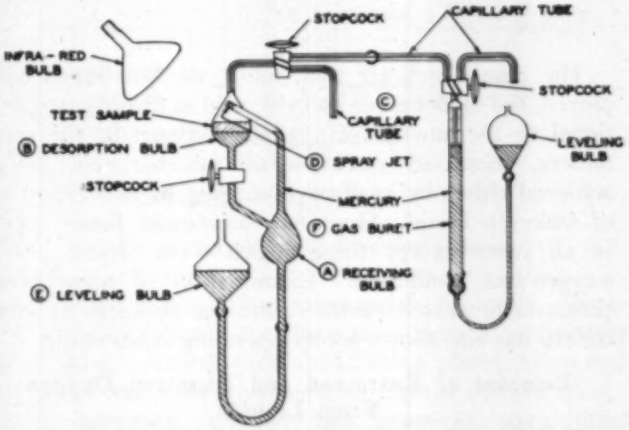



FIG. 1. Gasometric Equipment for Analysis of Dissolved Gases.

This portable equipment may be employed for determining headspace gas compositions by using the special sampling device shown in Figure 2. This unit consists essentially of an outer bonnet which is clamped into position by a ratchet arrangement, effecting an air-tight seal at the neoprene gasket on the upper surface of the sample can. The bonnet chamber is evacuated by connecting the sampling tube with the Toepler pump arrangement of the apparatus. After complete evacuation, the piercing needle is released to puncture the can. Headspace gases pass into the gasometric unit, where they are analyzed in the usual manner.

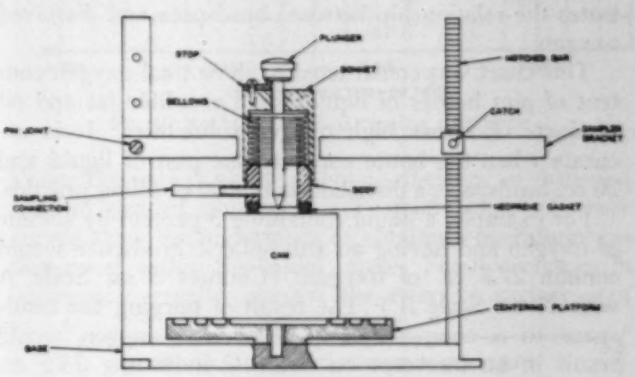



FIG. 2. Headspace Gas Sampler.

### Nomograph for Determining Relative Quantities of Dissolved and Headspace Gases

One of the principal applications of gas analytical techniques in the food industry is in the study of inert gas requirements for satisfactory food protection. To a great extent, present applications rely on purging methods in eliminating headspace oxygen at the time of container sealing. The effect of oxygen dissolved in the product prior to packaging is usually overlooked or underestimated. The nomograph in Figure 3 illus-

[a] Presented before the Ninth Annual I. F. T. Convention, San Francisco, California, July 13, 1949.

[b] Bayes, A. L., Flook, R. R., and Graham, G. B. *Food Industries*, 21, 310 (1949).

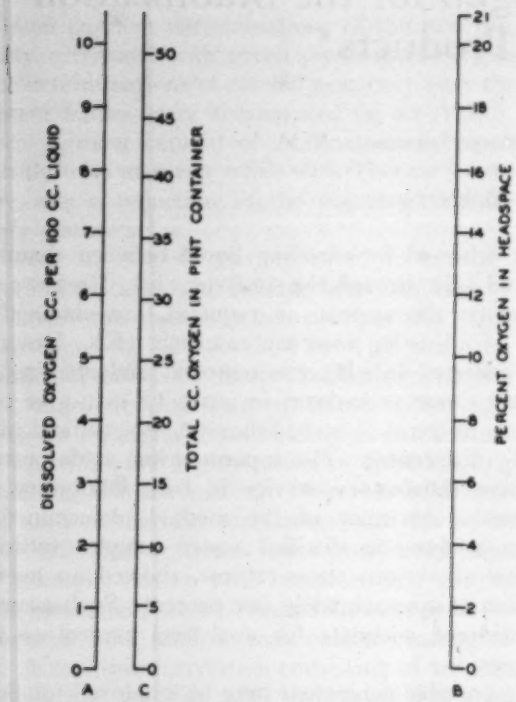



FIG. 3. Nomograph Showing Total Available Oxygen in Bottle Containing 1 Pint of Liquid Plus 20 cc. Headspace.

trates the relationship between headspace and dissolved oxygen.

This chart was constructed to show total oxygen content of pint bottles of liquids such as edible fat and oil products of rather high oxygen solubilities. It is accurate when the bottle contains one pint of liquid and 20 cc. headspace, a distribution typical of filling practice.

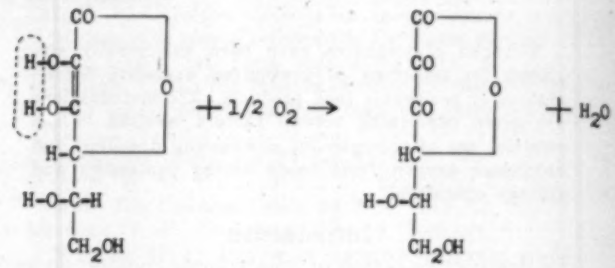
For example, a liquid containing 5 percent by volume of oxygen and having an atmospheric headspace would contain 27.7 cc. of oxygen. (Connect 5 on Scale A with 21 on Scale B.) The result of purging the headspace to a composition of 0 percent oxygen would result in an intercept on Scale C indicating 23.5 cc. contained oxygen. Thus, 4.2 cc., or about 15 percent of the total oxygen may be removed by headspace purging. The effect of reducing the dissolved oxygen content of the liquid may similarly be demonstrated by connecting 0 on the A-axis with 21 on the B-axis. In this case, it is found that the total oxygen content is reduced to only 4.2 cc. It is evident that in this case reduction of the dissolved oxygen content will contribute substantially more to the elimination of oxidative reactions than will variations of headspace compositions.

In aqueous-type liquids where the normal solubility of oxygen is in the range of 0.5 percent, the effects of headspace and dissolved oxygen are approximately equivalent. Nomograph charts have also been prepared to show similar relationships in other containers used in packaging food products.

### Effect of Oxygen on Stability of Ascorbic Acid

Such nomograph charts demonstrate the need for considering both product and headspace compositions in obtaining oxygen-free systems. This point is further emphasized by the effects of oxygen in ascorbic acid solutions prepared under controlled conditions. Ascorbic acid oxidizes according to the equation in Figure 4.

1 cc. oxygen is equivalent to 15.7 mg. ascorbic acid or, each cubic centimeter of oxygen destroys 15.7 mg. of ascorbic acid.




l - ascorbic acid dehydroascorbic acid

FIG. 4. Oxygen Equivalent for the Oxidation of Ascorbic Acid.

Losses of aqueous standardized solutions containing 100 mg. of ascorbic acid per pint were measured; Table 1 shows the results. The samples in pint bottles were stored for six weeks at 95° F., both solution and headspace oxygen content being determined at the time of packaging.

TABLE 1

*Relationship Between Available Oxygen and Ascorbic Acid Loss*

Initial Ascorbic Acid Content—100 mg./Pint
Storage Period—6 Weeks
Storage Temperature—95° F.

| Test No. | Available Oxygen | | | Final Ascorbic Acid Content | Ascorbic Acid Loss | |
|---|---|---|---|---|---|---|
| | Solution | Headspace | Total | | Exper. | Theor. |
| | *cc./100 cc.* | | *cc.* | *mg./pt.* | *mg.* | *mg.* |
| 1 | 0.53 | Air | 6.6 | 0 | 100 | 103.6 |
| 2 | 0.53 | Nitrogen | 2.4 | 58 | 42 | 37.7 |
| 3 | 0.01 | Air | 4.2 | 38 | 62 | 65.9 |
| 4 | 0.01 | Nitrogen | 0.0 | 97 | 3 | 0 |

The results indicate that, under the conditions employed, the depletion of ascorbic acid is directly proportional to the amount of available oxygen in the containers, increased retention of ascorbic acid being achieved either by headspace purging or deaeration of of make-up liquid. However, substantial losses occur in all cases except those which were stored under oxygen-free conditions. Examination of many food products processed under controlled atmospheric conditions has also shown a corresponding relationship.

### Removal of Entrained and Dissolved Oxygen From Liquids

Perishable liquid food products such as fruit and vegetable juices, milk, oils, wines, etc., often deteriorate in color, flavor, or nutritive value on exposure to air. The rates of deterioration are especially rapid during stages of processing or storage where high temperatures may be encountered. For this reason it is recommended that atmospheric exposure be minimized during commercial processing, although complete elimination of aeration is often impossible to achieve under practical conditions. In such cases, oxygen should be removed

from liquid systems as quickly and completely as possible by vacuum deaeration. This has already been widely adopted in the commercial processing of fruit juice.

As dissolved and entrained oxygen also may be removed from liquids by gas displacement methods, an experimental program was conducted to investigate the removal of oxygen from liquid systems by means of counter-current gas stripping operations.

Aerated solutions were introduced into the top of the column shown in Figure 5 by means of a device that

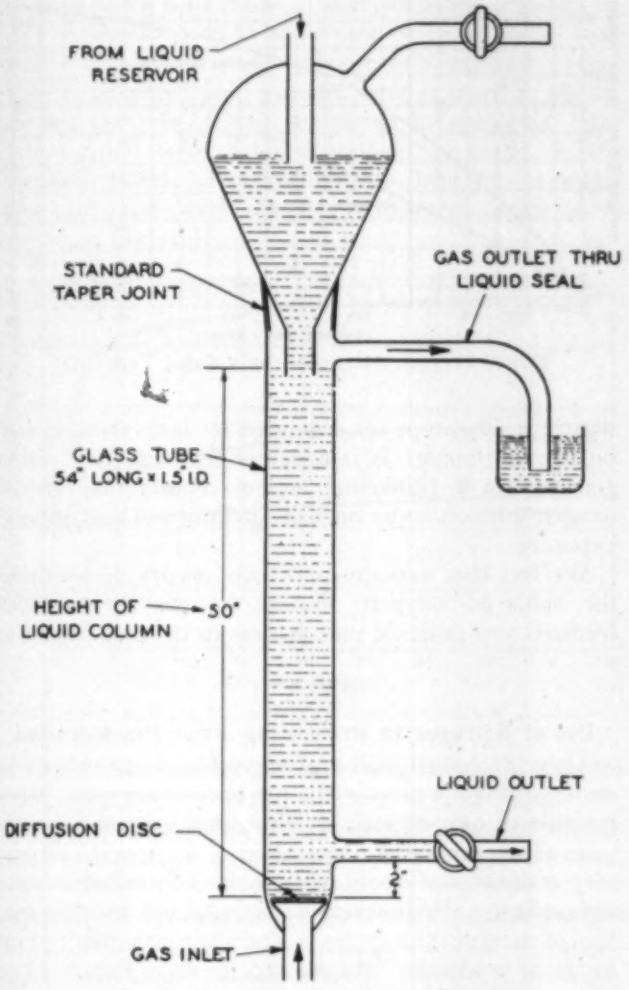



FIG. 5. Experimental Stripping Column.

maintained constant flow rates and liquid levels. Nitrogen was introduced into the bottom through a chamber containing removable jets or diffusion plates. Glass and stainless steel frits were used during the investigation.

In operation, column and reservoir were filled with aerated liquids, and desired flow rates established. After the nitrogen purging rate was adjusted, the system was allowed to operate continuously; samples were taken periodically to determine dissolved oxygen content. Attainment of equilibrium was noted by the constancy of oxygen analyses determined by a polarographic procedure calibrated for this purpose.

As would be expected, the stripping efficiency (oxygen removal per unit volume of gas consumption) of a deaeration system is proportional to the effective contact area of the gas-liquid interface. Optimum conditions were obtained by decreasing the bubble size of stripping gas, thereby effectively increasing the surface area of the gas phase. Satisfactory results were also obtained with column packing materials, which tended to increase the exposed liquid surface area. Figure 6

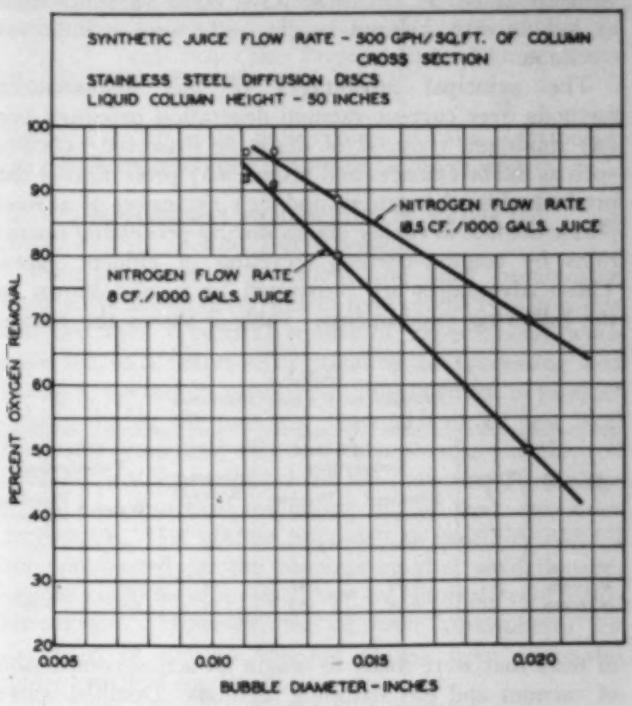



FIG. 6. Bubble Size vs. Stripping Efficiency.

shows the variations in stripping efficiency of diffusion frits of graded porosity. The steep slopes of these curves show the importance of obtaining maximum gas dispersion within the liquid phase. Small decreases in bubble size greatly increase the effective surface area

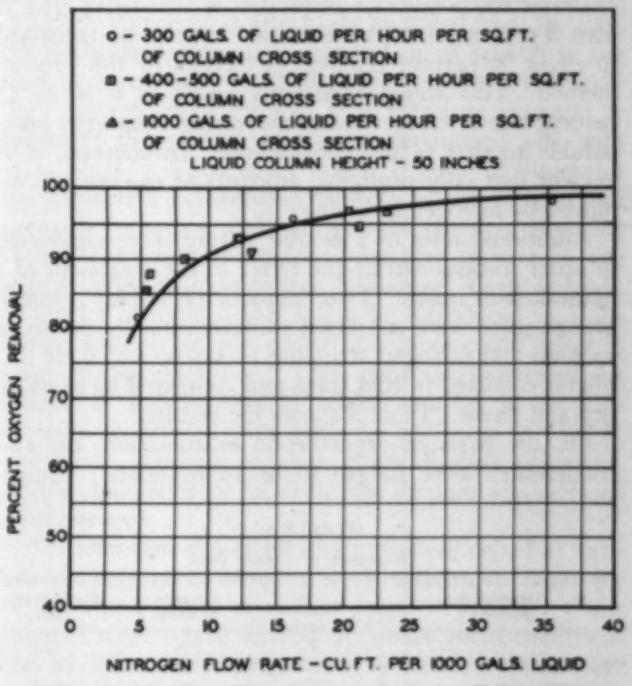



FIG. 7. Nitrogen Flow Rate vs. Stripping Efficiency.

and consequently enhance the attainment of equilibrium.

Results of experiments designed to show the relationship between oxygen removal and nitrogen consumption are summarized in Figure 7. Approximately 10 cu. ft. of nitrogen suffice to achieve 90 percent oxygen removal per 1000 gallons of aqueous solution initially saturated with air at 78° F. In these tests, other variables such as bubble size, column height, etc., were maintained constant.

The principal advantages of gas displacement methods over current vacuum deaeration processes are (a) minimum removal of desirable dissolved volatiles such as flavor essences and aroma, (b) protection of the product after deaeration, and (c) exclusion of atmospheric contact at earlier stages during processing operations by counter-current recycling of effluent gases. These advantages are illustrated by results shown in the following experiments. Table 2 shows the results

TABLE 2

*Nitrogen vs. Vacuum Deaeration*

| Method | Temp. ° F. | Original Liquid Composition | | Oxygen Removal | Loss by Vaporization | |
|---|---|---|---|---|---|---|
| | | Dissolved Oxygen | Propionaldehyde | | Water | Propionaldehyde |
| | | *cc./100 cc.* | *p.p.m.* | % | % | % |
| Vacuum | 104 | 0.42 | 35 | 55 | 1.6 | 5 |
| Vacuum | 104 | 0.38 | 140 | 58 | 1.6 | 8 |
| Nitrogen | 77 | 0.54 | 150 | 94 | 0.01 | 0.04 |

of tests that were made to obtain an actual comparison of vacuum and gas stripping methods. Distilled water was aerated at temperatures appropriate to each method, after which a known quantity of propionaldehyde (B. P. 118.8° F.) was added as a representative low-boiling essence material. Samples were then deaerated by means of vacuum and nitrogen stripping. Effluent gases from the deaeration apparatus were passed through liquid nitrogen traps for total condensate recovery.

Under the conditions employed, it is indicted that at least 3 percent of the water would have to be vaporized to effect 90 percent removal of oxygen by the vacuum method. This would apparently result in a 10 to 15 percent loss of essence materials having volatilities comparable to that of propionaldehyde. In contrast, it is evident that only negligible amounts of essence are removed by nitrogen stripping.

Additional tests of a similar nature were conducted in order to demonstrate the effect in the treatment of a natural fruit juice. Two aliquots of freshly reamed orange juice were subjected to deaeration by means of vacuum and nitrogen stripping methods, and their distillates collected in cold traps and compared as to quantity and flavor. Table 3 shows the results.

On the basis of organoleptic examination, the two condensates were judged to be approximately equivalent. It is evident that nitrogen stripping is more effective and results in less flavor loss than vacuum deaeration, which is common in present commercial practice.

TABLE 3

*Deaeration of Orange Juice*

| Deaeration Method | Temp. | Oxygen Removal | Condensate Loss |
|---|---|---|---|
| | ° F. | % | % |
| Vacuum | 104 | 77 | 1.8 |
| Nitrogen | 77 | 100 | 0.002 |

Under practical process conditions, the deaerated product may be exposed to atmospheric contact prior to packaging. The rate of oxygen pickup by the liquid then assumes considerable importance. Curves in Figure 8 indicate the comparative rates of oxygen solution in a salad-type oil deaerated by both vacuum and nitrogen stripping. It is apparent that dissolved nitrogen gas, in a blanketing action, retards the rate of oxygen solution under normal conditions of atmospheric exposure.

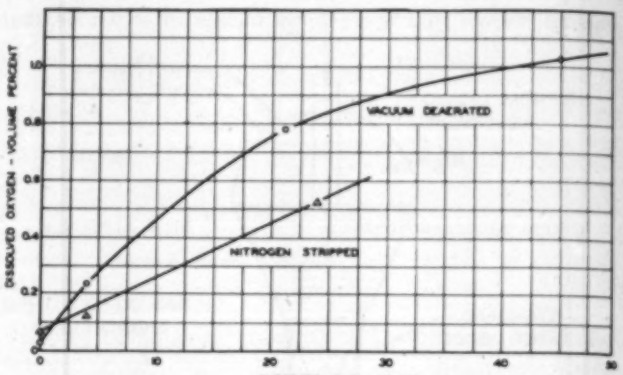



FIG. 8. Oxygen Absorption by a Salad Type Oil.

We feel that experimental-scale results demonstrate the value of oxygen removal by gas displacement methods as a practical unit-process in the food industry.

## PART II

### Use of Nitrogen in Preventing Food Discoloration

Many processed fruit and vegetable products tend to undergo discoloration in the presence of oxygen. Here the role of oxygen may be illustrated very well by results of experimental preparation of large-scale laboratory quantities of apple juice under controlled oxygen atmospheres. Preliminary tests indicated the elimination of oxygen at all stages prior to juicing as the critical factor in producing light colored juices. (Figure 9).

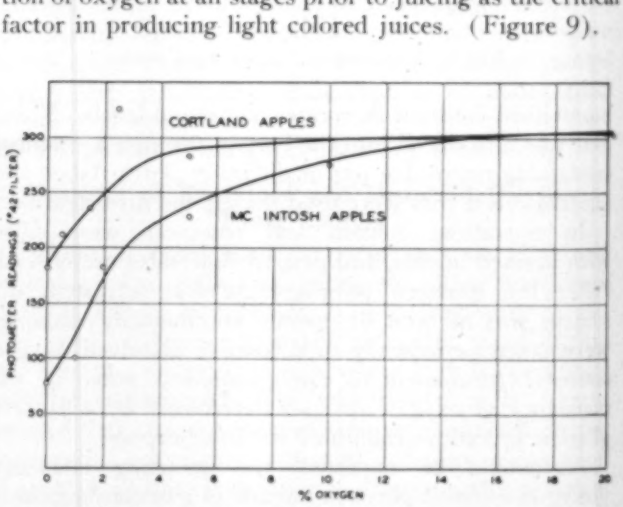



FIG. 9. Color vs. Composition of Pulping Atmosphere.

In these tests Cortland and McIntosh apples were pulped under atmospheres containing varying amounts of oxygen and pressed immediately in a small blanket-and-frame fruit press under atmospheric exposure. The samples were then treated with pectinol and stored at 35° F. for 24 hours under nitrogen headspace. With the use of a Klett-Summerson photometer with a No. 42 filter, the color intensity of final clarified samples of juice was found to be directly proportional to the amount of oxygen present in the pulping atmosphere.

Tests were also made to determine the stability or rate of discoloration of apple pulp prepared under controlled atmospheres and subsequently exposed to air. Freshly-prepared pulp samples were exposed to air for varying periods of time, extracted in open-type filter presses, and color determinations then made on the clarified juices. The relationship between exposure time and color development is represented by the curve shown in Figure 10.

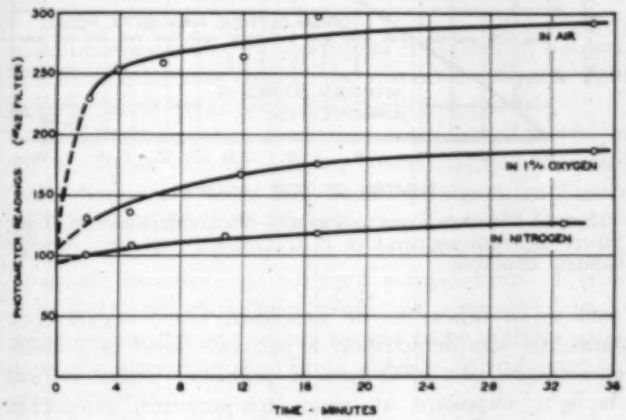



FIG. 10. Rate of Darkening of Pulped Cortland Apples.

Rapid discoloration of apple juice occurs in samples prepared under normal conditions of atmospheric exposure. Displacement of oxygen with nitrogen during pulping results in pulp that is relatively stable toward discoloration even upon subsequent exposure to the atmosphere. Comparison of the 0 and 1 percent oxygen curves indicates that even small quantities of oxygen cause substantial discoloration. Therefore, nitrogen application must be carefully controlled for best results in suppressing oxidation. It is evident that low oxygen levels must be maintained during pulping to obtain substantial color improvement. Experience has shown that clarified juices thus obtained will not darken even upon prolonged exposure to air.

Figure 11 shows apple pulp cakes that were prepared under air and nitrogen atmospheres, respectively. The normally processed cake is more or less uniformly colored, because of rapid oxidative reactions that occur during pulping when freshly-cut fruit cells are in intimate contact with air. The nitrogen-treated sample, however, shows only surface discoloration caused by subsequent contact with air. For practical applications, the ultimate color of juice produced from nitrogen-treated pulp will depend upon (a) time of air exposure before pressing, and (b) relationship between exposed

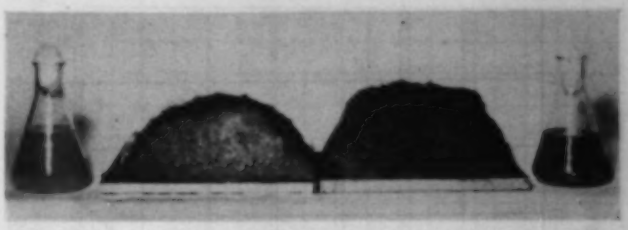


FIG. 11. Apple Pulp Cakes Prepared Under Nitrogen (left) and Air (right) Atmospheres.

surface area and total bulk volume of cake. Obviously, only the exposed outer layer will be discolored.

### Development of Rancidity in Edible Oil and Fat Products

Perhaps the most prevalent and most pronounced destructive action of oxygen in food products is in edible oils and fats. Practical results of experimental work have led to a better understanding of processing and handling operations resulting in improvement of product quality during the past few years. However, few food products containing oils and fats possess the desired shelf-life stability required for the reduction of spoilage losses to a practical minimum, or for peak consumer acceptance. The present approach to rancidity control was predicated on the assumption that oxidative reactions could be suppressed best by elimination of available oxygen. However, use of inert atmospheres for exclusion of oxygen has not always been successful under practical conditions.

Commercially, bland oils are produced under carefully controlled processing conditions. During final deodorization, all volatiles and dissolved gases are removed completely by steam stripping at relatively high temperatures and extremely low pressures. The oil at this point possesses its maximum chemical stability. Laboratory experiments have shown that freshly deodorized vegetable oils may be kept non-rancid indefinitely if oxygen is effectively excluded from the time the deodorizer vacuum is released, until sealing in the final storage container. Edible oils possess a relatively high oxygen solubility, and it is therefore essential to minimize the contact of freshly deodorized oils with atmospheric oxygen at all times. Figure 12 illustrates the theoretical relationship between active oxygen and peroxide formation and indicates the potential peroxide values that might result from dissolved oxygen in oils stored under an oxygen-free headspace. On this basis, quantities of oxygen that might be introduced into oils during commercial processing operations could result in poor storage qualities. This point is illustrated by laboratory experiments in which samples of soybean oil were deodorized with steam for six hours at 450° F. and 5 mm. absolute pressure in an all-glass apparatus. At the completion of the cycle, the vacuum was released with nitrogen.

To determine the effect of atmosphere on oil at various temperatures, samples were withdrawn from the $N_2$-blanketed vessel at various stages of cooling. Some samples were cooled to 100° F. under room conditions and stored in sealed glass tubes under air; others were cooled to 100° F. without exposure to air and placed

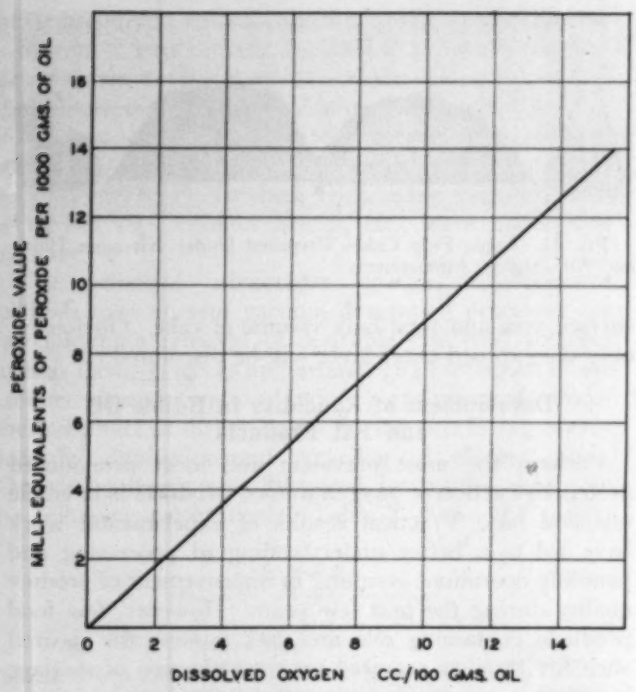

PEROXIDE VALUE
MILLI-EQUIVALENTS OF PEROXIDE PER 1000 GMS. OF OIL
0 2 4 6 8 10 12 14 16
DISSOLVED OXYGEN CC./100 GMS. OIL
0 2 4 6 8 10 12 14

FIG. 12. Theoretical Relationship Between Active Oxygen and Peroxide Value of Edible Oil.

in similar containers under nitrogen. All samples were then subjected to 48-hour accelerated storage under ultra-violet light, as well as four weeks under room conditions. Table 4 is an evaluation of these tests.

Sample No. 1, fully protected from atmospheric exposure, showed no oxidative deterioration either under normal or accelerated storage. Other samples increased in peroxide compositions, more or less, in proportion to the amount of oxygen present in the storage containers. It is interesting to note the rapid rate of peroxide formation in oils exposed to air at elevated temperatures. These results are typical of many similar investigations in which various bulk oil and fat products were used, and emphasize the fact that oxidative reactions causing rancidity may be suppressed by effective displacement of oxygen by nitrogen.

TABLE 4

*Effect of Oxygen on Soy Bean Oil Stability*

| Sample | Conditions of Air Exposure | | Initial Peroxide Value | Peroxide Value After Storage | |
|---|---|---|---|---|---|
| | Temp. ° F. | Cooling Time Hr. | | 48 Hr. Ultra-Violet 80° F. | 4-Wk. Normal Exp. 70° F. |
| 1 | ----[a] | ----[a] | < 0.10 | < 0.10 | < 0.10 |
| 2 | 100 | 0 | < 0.10 | 19.7 | 15.0 |
| 3 | 200 | 1.5 | 0.57 | 25.1 | 18.5 |
| 4 | 250 | 3.0 | 0.72 | 27.2 | 19.6 |

[a] No exposure.

The effect of storage atmospheres on the shelf-life of numerous commercial products such as peanuts, potato chips, mayonnaise, and shortening products has been investigated. In general, the results from investigation of effects of storage atmosphere on the stability of freshly roasted peanuts also apply to other oil- or fat-containing products. In this investigation, freshly roasted Virginia peanuts were packaged under controlled atmospheres in both rigid and flexible containers. Samples were stored under several conditions of temperature and light exposure and examined at intervals by organoleptic evaluations and chemical analysis for peroxide values.

Packaging peanuts in an oxygen-impermeable transparent-film under air and nitrogen atmospheres gave results shown in Figure 13. In this series of tests, as well as in others to be described later, organoleptic rancidity was detected at a peroxide level of 3 milli-equivalents per 1000 gm. of peanuts. Under normal daylight exposure at room temperature, air-packed samples had a non-rancid shelf-life of 4 weeks. On the basis of both chemical and flavor evaluation, the shelf-life of peanuts stored in transparent film containers under nitrogen depends on the ability of the packages to exclude oxygen. Because of limitations of the packaging film employed in this series of tests, oxygen-free atmospheres could not be maintained in the gas-packed samples for more than 10 weeks, after which peroxide development increased in proportion to the amount of oxygen penetration. Since the completion of this work, improved films have been made available. It is hoped that further developments in the field of protective packaging materials will be forthcoming in the near future.

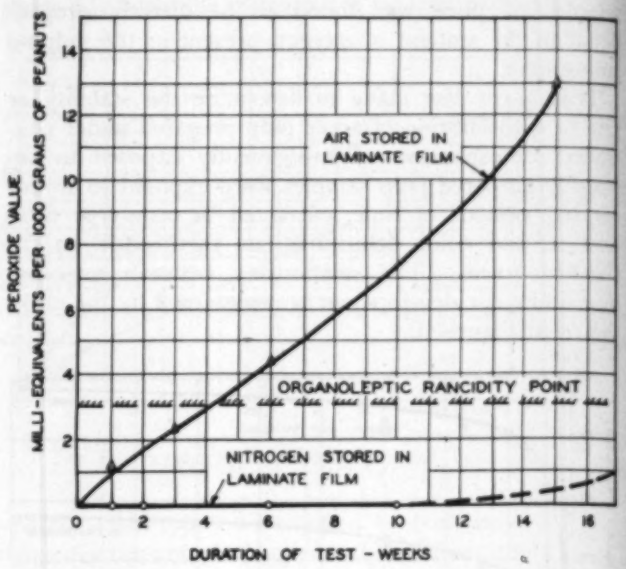

PEROXIDE VALUE
MILLI-EQUIVALENTS PER 1000 GRAMS OF PEANUTS
0 2 4 6 8 10 12 14
AIR STORED IN LAMINATE FILM
ORGANOLEPTIC RANCIDITY POINT
NITROGEN STORED IN LAMINATE FILM
0 2 4 6 8 10 12 14 16
DURATION OF TEST - WEEKS

FIG. 13. Storage Tests on Peanuts—Peroxide Value vs. Time. Stored at room temperature in transparent packages. Normal daylight exposure.

The effect of variations in storage conditions on the keeping qualities of peanuts packed in sealed glass containers is shown in Figure 14. It will be noted that, in the presence of air, ultra-violet light exerts a pronounced catalytic effect on the formation of peroxides. By comparing results at 70° F. under normal daylight exposure with those obtained at 95° F. in total darkness it is evident that light is a greater accelerating factor than temperature. Under all conditions of storage, nitrogen-packed samples remained unchanged in chemical or flavor qualities throughout the 16-week storage period. Later examinations showed these samples to be in excellent condition even after six months' addi-

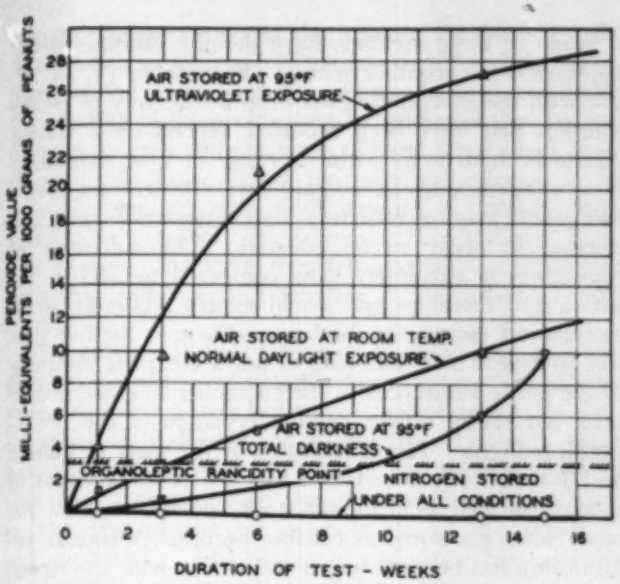



FIG. 14. Storage Tests on Peanuts—Peroxide Value vs. Time. Stored in glass containers in air and nitrogen.

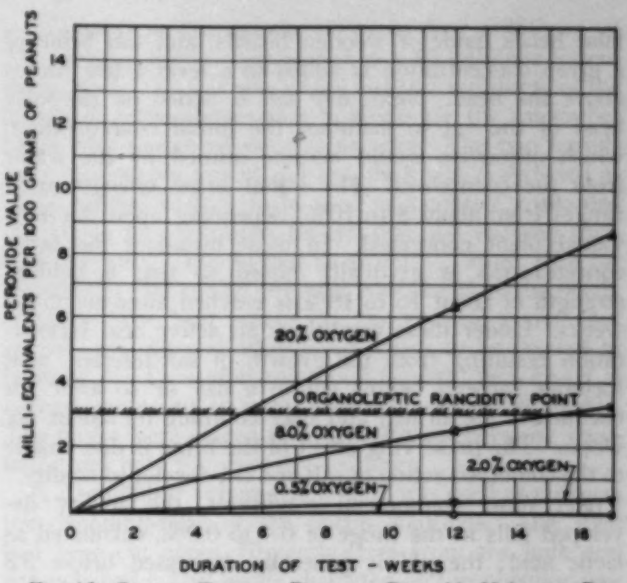



FIG. 15. Storage Tests on Peanuts—Peroxide Value vs. Percent Oxygen in the Packaging Atmosphere. Stored at room temperature in metal containers.

tional storage under all conditions employed in the test. The results indicate that, in the absence of oxygen, light is not a factor in the shelf-life stability of peanuts.

Rates of peroxide formation in peanuts stored at 70° F. under varying oxygen concentrations in sealed metal containers were determined as shown in Figure 15. Non-rancid shelf-life may be increased substantially by reducing the amount of available oxygen in the container atmosphere. Oxygen compositions of from 2 to 3 percent should be feasible in commercial packaging operations and would appear to be entirely satisfactory in maintaining product stability during extended storage periods.

### Conclusions

In general, the following were formulated as a result of this series of experimental studies:

A. Nitrogen may be used successfully for retarding or preventing quality deterioration (such as vitamin loss, discoloration, rancidity development) or other degradations that are due to the action of atmospheric oxygen.

B. Effective nitrogen processing techniques depend upon careful analytical control of oxygen compositions during all stages of processing and packaging. The influence of dissolved gases must not be overlooked in recommending procedures for commercial applications.

C. Gas displacement methods are both effective and advantageous for removing dissolved and entrained oxygen from liquid materials. The counter-current stripping procedure promises to be a valuable new unit-process in the food industry.

# Softening of Commercial Cucumber Salt-Stock in Relation to Polygalacturonase Activity[a]

THOMAS A. BELL,[b] JOHN L. ETCHELLS,[b] AND IVAN D. JONES[c]

(Received for publication, October 17, 1949)

**A sensitive method is described for detecting a pectin-splitting enzyme in commercial cucumber brines. The enzyme compares similarly in chemical behavior to polygalacturonase and has been found present in cucumber brines from various brining areas and correlated with softening of the salt-stock.**

During the brine fermentation of cucumbers for manufacture of pickles, the industry is often faced with an uncontrollable problem of spoilage known as "softening." At such times the cucumbers, referred to as salt-stock, soften to a varying extent. They may either lose their firmness completely, becoming mushy; or they may develop softening to such a minor degree that it is hardly noticeable even to an experienced plant operator. In some years, the spoilage is far more serious and widespread than in others. The economic loss to the industry is considerable when soft salt-stock has to be discarded or, at best, used in low-quality products.

The commercial brining operation has been described *(5)* as follows: "The cucumbers are brined in wooden vats ranging in capacity from 100 to 1,200 bushels. The vats, after being filled with cucumbers, are fitted with

[a] Agricultural Chemical Research Division Contribution No. 248. Aproved for publication as paper No. 320, of the Journal Series of the North Carolina Agricultural Experiment Station.

[b] Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Raleigh, N. C.

[c] Department of Horticulture, North Carolina State College, Raleigh, N. C.

false heads made of wooden boards, and salt brine of a given concentration is added to a level a few inches above the head. Next, dry salt is added on the false head of the vat to maintain the initial concentration, which otherwise would become diluted by the water from the cucumbers. The initial brine strength used ranges from about 8 to 10%, depending upon the individual plant concerned. In most instances the brine concentration is gradually raised so that a holding strength of about 16 to 18% is reached after about six weeks. Under these conditions an active acid fermentation resulting from the growth of salt-tolerant, acid forming bacteria begins within a day or so after the cucumbers are brined and may continue for about six weeks. The preserving effect of the brine is due chiefly to the combined action of salt and the developed acidity." Under most commercial conditions, the acidity developed falls in the range of 0.4 to 0.9%, calculated as lactic acid; the pH is generally depressed below 3.8 *(5, 11)*.

It is generally accepted that softening is seldom detected until after the active fermentation period. The softening action has been considered to be the result of action by pectin-splitting enzymes on the pectin composing the middle lamella of cucumber tissue. The chemistry of pectin and its association in fruits and vegetables has recently been the subject of three review articles *(2, 13, 19)*. Phaff and Joslyn *(21)*, in their review on pectic enzymes, concluded that there were two principal types; pectinesterase (*syn.* pectase) which catalyzes the de-esterification of pectin by removal of the methoxyl groups, and polygalacturonase (*syn.* pectinase) which catalyzes the glycosidic hydrolysis of pectin or pectic acid.

The present study considers principally the detection of pectin-destroying enzymes in commercial cucumber fermentations. There was no information found in the literature dealing with softening of cucumbers brined under commercial conditions and the enzymes involved. A method which would permit the early detection of such enzyme systems would prove valuable for the pickle industry for it would permit the early forecasting of the probable final quality of salt-stock. Likewise such a method would benefit the bacteriologist conducting research in brine fermentations for it would serve as a measure of the softening activity of organisms encountered. For the chemist in fermentation research, the proposed method would aid in developing softening control procedures. The enzyme responsible for the destruction of pectin is polygalacturonase; hence, at the start of these experiments polygalacturonase was considered to be associated with cucumber softening. The results to follow substantiate this assumption.

## Selection of Method

Phaff and Joslyn *(21)* list five general methods for measuring activity of polygalacturonase on pectin solutions: Increase in reducing substances measured as aldoses; decrease in calcium pectate precipitate; decrease in alcohol precipitate; marked drop in viscosity of pectin solution; and decrease in optical rotation.

Some of these methods have definite limitations for application to cucumber brines. The methods *(9, 16, 17, 23)* with the exception of the drop in viscosity of pectin solution that have been reported depend on a strong glycosidic hydrolysis within a range of time extending from a few minutes to several hours. Hydrolysis at this rate would require relatively high concentrations of the enzyme in order to be effective. The softening of cucumbers is extremely slow compared to such a reaction and therefore one would expect relatively small amounts of enzyme in the brine. There is further reason to believe that softening is not a complete splitting of the pectic substances in the cucumber to galacturonic acid, but rather only a depolymerization of the protopectin molecule. This is indicated by the work of Fabian and Johnson *(6)* who found that the pectin content of mushy, as well as firm salt-stock cucumbers, was the same when measured as calcium pectate. A similar relationship has been shown in connection with the ripening and softening of peaches *(1)*.

Jansen and MacDonnell *(9)*, studying the change in viscosity of pectin by polygalacturonase, reported that a 50% change in viscosity of a 1.0% pectin solution hydrolyzed by the enzyme, or by heat, occurs with only a 2% breakage of the glycosidic bonds. Kertesz *(14)* observed that a 1% hydrolysis by the enzyme on a pectin solution would cause about 35% reduction in the viscosity. He pointed out that the decrease in viscosity was more rapid than the increase of aldehydic reducing groups. Viscosity changes of a 1% pectin solution was used by Mottern and Hills *(17)* as a measurement of the enzyme activity in tomato extract.

At the start of the present work several workers *(3, 12, 22)* in the field of pectin and pectic enzymes suggested that the viscosity method might prove the most satisfactory for indicating low concentrations of the enzymes. Principal emphasis has been placed on developing such a method for brines, although the method described by Jansen and MacDonnell *(9)* for measuring liberated aldehydic groups as aldoses was also investigated. This method was more accurate than the viscosity method and more specific for high concentrations of the enzyme, but it was found that there was not sufficient enzyme in a polygalacturonase-active brine to give a measurable reduction of a standard iodine solution using either pectin or pectic acid. It was evident from these observations that this method was not suitable for the present work. Details of the work with this method are therefore not included in this report.

## Viscosity Method of Measurement

*Materials.* The pectin[4] used in the experiments described was a commercial citrus product of highest quality, recommended by the research staff *(12)* of the California Fruit Growers Exchange as the most desirable material for the work. The polygalacturonase

[4] Obtained from California Fruit Growers Exchange, Ontario, California, under the name "Pectinum NF VIII." Analysis: Free of sugars; hydrolyses to galacturonic acid, 88-90%; methoxyl 9.7%, and pH 3.7 to 4.0. A pectin suitable for enzyme test in pickle brines should be specified.

enzyme system used was the product Pectinol M*. As this product contains 90% glucose as diluent the quantities of the enzyme in the standards were one-tenth the quantity of the product used. Studies of the Pectinol enzyme by Fish and Dustman *(7)* and Jansen and MacDonnell *(9)* have shown the principal enzyme to be polygalacturonase with small amount of pectinesterase being also present. More recently Lineweaver, Jang, and Jansen *(15)* have reported several more enzymes including cellulase and amylase to be present in the Pectinols.

*Procedure.* Pectin solutions of low concentrations exhibit viscosities of relative large value. The pectin molecule being a high polymer of galacturonic acid may serve as an indicator for measuring extremely small quantities of polygalacturonase. The method used in this study was essentially that of measuring the decrease in the size of the pectin molecule as the result of enzyme activity. The change in viscosity offers a means of measuring the extent of depolymerization.

Studies of the effect of the concentration, temperature, pH, and presence of salts on the viscosity of pectin solutions have demonstrated *(4, 18)* that the viscosity of dilute solutions increases with concentration to 0.5%, and also increases with decreasing temperatures. Further, the viscosity was found to be at the minimum at pH 6. On the basis of previous work, it was recognized that it would be necessary to buffer the pectin solution at the desired pH, and to control temperature and the concentration of pectin to insure accurate viscosity measurements.

*Pectin solution.* A 3% pectin solution yielding a relative viscosity about 40 was used as a standard. It was prepared in 0.5N sodium citrate—citric acid buffer solution at pH 4.0. The buffer solution was heated to 50° C.; the pectin was added gradually during mixing with an electric stirrer; and the suspension was then treated 1 minute in a Waring Blendor. To insure uniformity the solution was passed through several thicknesses of cheesecloth. Microbial growth was inhibited by the addition of 0.1 milliliter of toluene to each 100 milliliters of solution which was stored in a tightly stoppered flask in the refrigerator at 5° C.

*Polygalacturonase standard solutions.* These were prepared from accurately weighed quantities of commercial Pectinol. A 10,000 microgram per milliliter (1.0%) solution in distilled water was prepared freshly each time and proper dilution standards were made for each desired concentration.

*Cucumber brines.* Samples were taken from vats of fermenting cucumbers at commercial salting stations with the aid of a stainless steel tube reaching to the approximate center of the vat. They were stored in bottles of approximately 250-milliliter capacity, preserved with 0.5 milliliter toluene, and held at 5° C. The polygalacturonase-active brine used in most of the experiments is designated as H-10.

*Viscosity measurements.* Twenty-five milliliters of 3% pectin solution were placed in a 50-milliliter Erlenmeyer flask. To this was added either 5 milliliters of the standard polygalacturonase solution or the cucumber brine with suspected enzyme activity. The two liquids were thoroughly mixed and this flask was designated as *A*. A second flask *B*, to be used as a control, contained the above two solutions except that the enzyme solution (or brine) was heated in an 80° C. water bath for 10 minutes and cooled before it was placed in the pectin solution. The heat inactivates the enzyme system but permits the salt and other constituents to be present as in flask A. To inhibit microbial growth, two drops of toluene were put in each flask and stoppered tightly. The flasks were placed in a constant tmeperature incubator and held for viscosity readings.

A 20-milliliter volumetric pipette was used to measure the dropping-time of the pectin solutions. The stem had been cut about 10 centimeters from the bulb and fire-polished. The inside diameter of the opening was 2.11 millimeters and the dropping time, measured with an electric precision stop-clock, was 0.05 minutes for water as compared to an average 2.00 minutes for 3% pectin solution. The pectin solution was drawn into the pipette with a rubber suction bulb attached to the top. The flow time was measured from the graduation mark on the upper stem to an etched mark 5 millimeters from the bulb on the lower stem. This pipette was easily cleaned and dried between each viscosity reading with hot water, ethyl alcohol, and acetone. (See Figure 1).

FIG. 1. Apparatus for determining viscosity of pectin solution showing pipette with suction bulb attached. Flask A contains pectin solution plus enzyme solution and flask B pectin solution plus heated enzyme solution. The hot water, waste alcohol, and acetone are used in order listed to clean and dry the pipette between each viscosity measurement. The stop-watch (or an electric precision stop-clock) is used to measure the flow time of pectin solution from the pipette.

* Pectinol M is a commercial enzyme manufactured and supplied by the Röhm and Haas Company, Philadelphia, Pa.

Mention of trade products does not imply that they are endorsed or recommended by the Department of Agriculture over similar products not mentioned.

The pectin solution — enzyme solution mixtures (Flasks A and B) were brought to a temperature of 26° C. in a constant temperature bath and viscosities were read at 26° C. ± 1° C. The equipment permitted making measurements with such speed and accuracy that reading time variation was within ± 0.01 of a minute.

The activity of the polygalacturonase is expressed as a loss in viscosity of the pectin and active enzyme solution mixture, A, over the pectin and inactive enzyme solution mixture, B, calculated as follows:

$$\frac{(B - A)}{B} \times 100 = \text{Percent loss in viscosity}$$

The results of using different concentrations of polygalacturonase ranging from 0 to 4.00 micrograms per milliliter are shown in Table 1. The reactions were at

TABLE 1

*Effect of Polygalacturonase on the Viscosity of Pectin Solution Buffered at pH 4.0 and Incubated at 30° C.*

| Polygalacturonase* | Loss in Viscosity | |
|---|---|---|
| | 3-day Incubation | 6-day Incubation |
| *μ per ml.* | *percent* | *percent* |
| 0.00 | 0 | 0 |
| 0.04 | 2 | 7 |
| 0.08 | 9 | 14 |
| 0.12 | 15 | 19 |
| 0.16 | 17 | 25 |
| 0.20 | 19 | 29 |
| 0.40 | 23 | 35 |
| 0.60 | 28 | 38 |
| 0.80 | 32 | 43 |
| 1.20 | 39 | 47 |
| 1.60 | 41 | 51 |
| 2.00 | 46 | 55 |
| 2.50 | 46 | 56 |
| 3.00 | 48 | 59 |
| 4.00 | 52 | 62 |

* Reaction mixture; 5 ml. enzyme solution and 25 ml. of 3% pectin solution, average relative viscosity of heated control, 30.3.

30° C. temperature and buffered at pH 4.0, and the viscosities were determined after 3- and 6-day incubation periods. A definite rate of change in the viscosity was observed with these levels of enzyme solution but the relation was not linear. For example, a 6-day incubation using 0.12 microgram of polygalacturonase

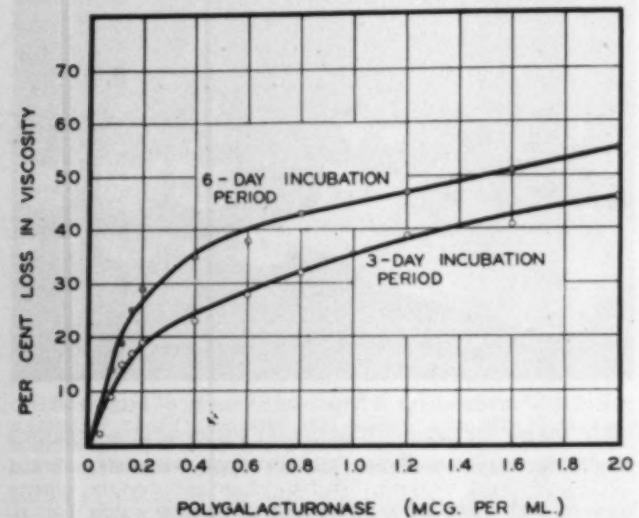



FIG. 2. Effect of polygalacturonase (Pectinol M) on the viscosity of pectin solution.

standard gave a change in viscosity of 19% whereas 5 times that amount, 0.60 microgram, gave 38%, only twice that change in viscosity. Figure 2 is a graphic presentation of the data in Table 1. A sharp break in the viscosity curve was noted between 0.20 and 0.40 microgram per milliliter enzyme solution. The most accurate part of the curve was that between 0 and 0.20 microgram enzyme solution using the 6-day incubation period.

Four concentrations of the "active" cucumber brine (H-10), shown in Table 2, gave results similar to those

TABLE 2

*Effect of Various Concentrations of Cucumber Brine, H-10 on the Viscosity of Pectin Solution, Buffered at pH 4.0 and Incubated at 30° C.*

| Cucumber Brine (H-10)* | Water Added | Loss in Viscosity |
|---|---|---|
| *ml.* | *ml.* | *percent* |
| 1 | 4 | 20 |
| 2 | 3 | 28 |
| 4 | 1 | 32 |
| 5 | 0 | 38 |

*Reaction mixture contained 5 ml. brine-water solution and 25 ml. of 3% buffered pectin solution.

for standard polygalacturonase. The percent change in viscosity was 20% for 1 milliliter of brine diluted to 5 with water and was 38% for an undiluted 5 milliliter sample. The reaction mixture, as to pH, pectin concentration, incubation temperature and time, was the same as for the standard polygalacturonase.

## Factors Influencing Enzyme Activity and Relative Viscosity

*Influence of temperature and period of incubation.* The effect of 20°, 30°, and 40° C., incubation temperatures and length of time ranging from 1 to 10 days was observed on both the commercial polygalacturonase and the "active" cucumber brine (H-10). As shown in Table 3 the loss in viscosity increased with the length of

TABLE 3

*Influence of Temperature, and Incubation Period on Enzyme Activity of Polygalacturonase and "Active" Cucumber Brine in Pectin Solution*

| Enzyme | Incubation Time | Loss in Viscosity* | | |
|---|---|---|---|---|
| | | Incubation Temperature | | |
| | | 20° C. | 30° C. | 40° C. |
| | *days* | *percent* | *percent* | *percent* |
| Polygalacturonase (2.00 microgram per milliliter) | 0 | 0 | 0 | 0 |
| | 1 | 23 | 23 | 24 |
| | 3 | 32 | 46 | 39 |
| | 6 | 44 | 56 | 53 |
| | 10 | 50 | 62 | 56 |
| "Active" Cucumber Brine (H-10) | 0 | 0 | 0 | 0 |
| | 1 | 5 | 12 | 17 |
| | 3 | 14 | 29 | 28 |
| | 6 | 27 | 39 | 39 |
| | 10 | 30 | 57 | 53 |

*Reaction mixture, 5 ml. enzyme solution and 25 ml. 3% pectin solution, at pH 4.

incubation time for both enzyme systems. The 30° C. incubation temperature favored greater viscosity loss than the 20° or 40° C.; yet there was not too great a difference between the 30° and 40° C. temperatures.

It was observed that depolymerization may occur due to the influence of temperature in the absence of enzymic

activity. This degradation would not introduce a large error as the results are based on a ratio of two pectin solutions held at the same temperature. It was found that in a 10-day incubation period, a pectin solution with relative viscosity of 43 lost 1% at 20° C., 3% at 30° C., and 18% at 40° C. Even though this loss in viscosity was compensated, it was not considered desirable to use the 40° C. incubation temperature. Because of these observations, a 6-day incubation period at 30° C. was adopted for measuring the enzymic activity.

*Adjustment of pH.* Five different pH levels were tested with the buffered citrate-citric acid-pectin solution. The results are given in Table 4 for polygalacturonase and "active" brine (H-10). The relative viscosity decreased as the pH of the solutions was increased from 2.5 to 6.3. Similar results are reported by other investigators *(4, 18)*. The maximum change in viscosity caused by polygalacturonase and brine enzyme occurred at pH 4.0, which was approximately the same as the optimum pH given by others *(16, 20, 21, 22)*. From the results it was evident that the enzyme in the brine and the commercial polygalacturonase responded in the same manner to pH adjustment.

TABLE 4

*Effect of pH on Loss in Viscosity of Pectin Solution by Polygalacturonase and Active Cucumber Brine (Vat H-10)*

| pH | Relative Viscosity[1] | Loss in Viscosity* Polygalacturonase (μ per ml.) 0.04 | 0.20 | 2.00 | pH | Relative Viscosity[1] | Loss in Viscosity* Active Brine Vat H-10 |
|---|---|---|---|---|---|---|---|
| | | *percent* | *percent* | *percent* | | | *percent* |
| 2.5 | 48 | 6 | 18 | 47 | 2.7 | 60 | 22 |
| 4.0 | 30 | 8 | 28 | 54 | 3.7 | 39 | 38 |
| 5.0 | 29 | 4 | 16 | 44 | 4.5 | 35 | 39 |
| 5.8 | 25 | 3 | 7 | 37 | 5.3 | 34 | 37 |
| 6.3 | 18 | 2 | 6 | 25 | 5.5 | 29 | 28 |

* Incubation time 6 days at 30° C.; reaction mixture contained 5 ml. enzyme solution and 25 ml. 3% pectin solution.
[1] Viscosity of flask B.

*Influence of Sodium Chloride.* Pallman et al. *(20)* observed that a number of chloride salts in low concentrations activated polygalacturonase. They further found that the maximum activity was obtained at 3.0 milliequivalents (0.017% NaCl) regardless of whether sodium or potassium chloride was used. In cucumber fermentations, the salt concentration may range from 5 to 18% by weight.

Tests were made to study the effect of 0, 5, 10, 15 and 20% sodium chloride solutions on the viscosity of pectin, and on the activity of 0.20 and 2.00 micrograms per milliliter of polygalacturonase upon pectin. The data given in Table 5 confirm other reports *(4, 18)* that increasing salt concentration raises the relative viscosity of the pectin solution. The loss in viscosity is markedly reduced at the 0.20 microgram per milliliter level of the enzyme in salt solutions greater than 10%.

In a second experiment (reported also in Table 5), a cucumber brine was inactivated by heat and polygalacturonase at two levels was added; 0.20 and 2.00 micrograms per milliliter. The cucumber brine contained 16% salt and the results are very similar to the salt-enzyme solution test.

TABLE 5

*Influence of Salt on the Viscosity of 3 Percent Pectin Solution With and Without Polygalacturonase, and Upon Heated Cucumber Brine With the Enzyme**

| Sodium chloride concentration[1] | Relative viscosity of Pectin Solution | Loss in Viscosity Polygalacturonase μ/ml. 0.20 | 2.00 |
|---|---|---|---|
| *percent by wt.* | | *percent* | *percent* |
| 0 | 26 | 29 | 54 |
| 5 (20°)** | 27 | 28 | 55 |
| 10 (40°) | 33 | 16 | 52 |
| 15 (58°) | 37 | 10 | 46 |
| 20 (75°) | 40 | 8 | 39 |
| F-271 Cucumber Brine | | | |
| 16 (60°) | 42 | 12 | 38 |

* Incubation time 6 days at 30° C. reaction mixture contained 5 ml. enzyme solution and 25 ml. 3% pectin solution.
[1] Standard polygalacturonase solution prepared with salt solutions or brine to desired concentrations.
** Salometer equivalents as percent saturation with sodium chloride.

In a third experiment an "active" cucumber brine (H-10) was increased in salt content from 13.3% to 21.3% (50° to 80° sal.). The loss in viscosity at 13.3% salt was 40% as compared to 42% with 21.3% salt.

These observations show that high concentrations of salt will not inactivate or precipitate polygalacturonase. This is in disagreement with the report by Fabian and Johnson *(6)* who concluded that the enzymes [protopectinase which is closely related to polygalacturonase *(21)*, and pectase] produced by *B. mesentericus fuscus* became inactive in salt concentrations above 2 or 3%. It is doubtful whether they were working with the polygalacturonase enzyme that is found in commercial cucumber brines.

*Pectinesterase in cucumber fermentations.* During the testing of brines for polygalacturonase activity it was observed that in a number of cases a gel formed in the flask containing pectin solution plus unheated brine (Flask A) but that no gel was ever found in the pectin solution mixtures plus heated brine (Flask B). The gel formation was attributed to the action of pectinesterase which de-esterifies the pectin and to the presence of polyvalent cations.

A further test for the esterase was made by the examination of several brines using the method of Hills and Mottern *(8)*. Brine F-100, with negative polygalacturonase activity, contained 16 times the amount of the esterase as the active polygalacturonase brine (H-10). The following values expressed as milligrams methoxyl per 30 minutes per milliliter were obtained: Cucumber brine F-100, 1.0; cucumber brine H-10, 0.06; fresh tomato extract (high in pectinesterase) 14.6. It has been reported *(9)* that partial de-esterification must take place before glycosidic hydrolysis, and the simultaneous action of polygalacturonase and pectinesterase will speed the glycosidic hydrolysis of the pectin. Since no attempt has been made to separate the two enzymes in this study, the speed of the reactions cannot be taken as a measurement of polygalacturonase but a measurement of pectin-hydrolysis. The objective of the study was to correlate pectic enzymes in the fermentations to softening of cucumber salt-stock. Further, it

has been shown *(10)* that high concentrations of crude pectinesterase caused inhibition of the polygalacturonase. However, this inhibitory effect was not noticed with the purified esterase. The "gel" brines reported in the present study indicate that when calcium or polyvalent cations are present the naturally occurring esterase may exhibit an inhibitory effect on polygalacturonase action (see addendum).

An interesting observation was made with several vats of cucumbers that were extremely moldy when brined. Mold growth occurred during transportation of fresh cucumbers that were improperly refrigerated in transit. A polygalacturonase viscosity test made 1 day after cucumber salting indicated a very high enzyme activity. The enzyme activity dropped to a very weak test on a 2-day sample and a 3-day sample gave a firm gel test. After a 3-month curing period, the cucumber salt-stock from these vats was very firm in texture thereby substantiating the opinion that polygalacturonase activity was not pronounced.

### Addition of Polygalacturonase to Cured, Commercial Salt-Stock

Polygalacturonase from Pectinol (200 $\mu$/ml. brine) was added to cured, cucumber salt-stock which was approximately 1 year old. This material was considered very firm and had an average pressure test, as indicated by the USDA fruit tester, of 18. The salt-stock brine was at pH 4.0 and 18% salt. The enzyme reduced the firmness of the stock 50% in 42 days and 66% in 62 days as compared to the control. This was evidence that polygalacturonase will soften commercially cured cucumber salt-stock.

As the Pectinols contain other enzymes *(15)*, a purified polygalacturonase, supplied by Mr. E. F. Jansen of the Western Regional Research Laboratory, Albany, California, was also added to salt-stock (4 $\mu$/ml.) and produced softening.

### Polygalacturonase in Commercial Cucumber Brines

Twenty fermentations, representing six commercial pickling plants in five southern states, were tested for polygalacturonase activity using the viscosity method. The results given in Table 6 were typical of the range in activity of 239 commercial vat fermentations studied. They represented considerable variation in cucumber sizes, cucumber varieties, vat capacities, salt treatments, ages of fermentations, and acid production. Fourteen of the 20 brines gave positive loss in viscosity of the pectin solution. The firmness of cucumber salt-stock from the 14 vats ranged from soft and mushy to only a slight loss in firmness as indicated by the USDA fruit pressure tester. The salt-stock from the six polygalacturonase-negative vats was of very good quality with respect to firmness. Summary of enzyme activity of commercial brines is given in Table 7.

TABLE 6

*Correlation of Polygalacturonase Activity in Commercial Cucumber Fermentations With Salt-Stock Firmness*

| Plant and Vat No. | Fermentation Age | Polygalacturonase Activity Measured by Loss in Viscosity of Pectin Solution | Firmness of Cucumber Salt-Stock* | Chemical Properties of the Brines | | | Chemical Properties of the Brines | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Salt Concentration | pH | Total Acidity as Lactic | Vat Capacity | Variety | Size †† |
| Plant F.† | *days* | *percent* | *pounds* | *percent* | | *percent* | *bushels* | | |
| 139 1 | 27 | 54 | 7 | 15 | 3.30 | 0.80 | | Producer | 1's and 2's |
| 2 | 46 | 43 | | 17 | 3.40 | 0.78 | | | |
| 271 1 | 41 | 33 | 8 | 16 | 3.50 | 0.42 | | Producer | 1's and 2's |
| 2 | 60 | 19 | | 18 | 3.45 | 0.35 | | | |
| 262 1 | 43 | 0 | 16 | 16 | 3.85 | 0.28 | (600-800) | Producer | 1's and 2's |
| 2 | 62 | 0 | | 18 | 3.95 | 0.28 | | | |
| 100 1 | 43 | 0 | 16 | 17 | 4.00 | 0.27 | | Producer | 1's and 2's |
| 2 | 75 | 0 | | 18 | 4.10 | 0.26 | | | |
| Plant C. | | | | | | | | | |
| H2 | 26 | 33 | Mushy | 13 | 3.50 | 0.72 | 700 | Producer | 1's |
| H10 | 30 | 39 | Mushy | 13 | 3.45 | 0.80 | 700 | Producer | 1's |
| G42 | 32 | 38 | Mushy | 14 | 3.40 | 0.65 | 700 | Producer | 1's |
| G58 | 30 | 21 | Mushy | 14 | 3.40 | 0.73 | 700 | Producer | 1's |
| Plant O. | | | | | | | | | |
| 20-18 | 69 | 0 | 20 | 19 | 3.90 | 0.42 | 1000 | Producer and Model | Mixed |
| 21-3 | 80 | 0 | 18 | 19 | 4.00 | 0.28 | 400 | Earliest of All | Mixed |
| 21-14 | 80 | 0 | 16 | 19 | 4.20 | 0.31 | 800 | Producer and Model | Mixed |
| Plant T. | | | | | | | | | |
| 10** | 132 | 8 | 8 | 18 | 3.25 | 0.51 | 500 | National and Model | Mixed |
| 115** | 60 | 7 | 13 | 14 | 3.20 | 0.82 | 500 | National | 2's |
| 77 | 96 | 0 | 17 | 16 | 3.30 | 0.81 | 500 | National | 1's and 2's |
| Plant W. | | | | | | | | | |
| 252** | 122 | 9 | Mushy | 20 | 3.12 | 0.44 | 700 | National | 1's and 2's |
| 126 | 135 | 4 | 11 | 21 | 2.85 | 0.98 | 700 | Model | 1's and 2's |
| 124 | 134 | 1 | 13 | 19 | 3.15 | 0.62 | 700 | Model | 1's and 2's |
| Plant M. | | | | | | | | | |
| 401 | 111 | 13 | 12 | 17 | 3.30 | 0.74 | 600 | ——— | 1's and 2's |
| 504 | 87 | 5 | 11 | 17 | 3.20 | 0.59 | 600 | Producer | Mixed |
| 210 | 117 | 2 | 13 | 18 | 3.30 | 0.48 | 210 | Model | 2's and 3's |

* Firmness indicated in pounds resistance using USDA fruit tester with 5/16 inch tip. Values represent average of 10 cucumbers No. 2 size (1⅝ to 1½ inches diameter) tested at stem and blossom ends for each lot. Values 16 to 20 pounds are considered firm and values of 13 and below inferior. All lots pressure tested after a 2 to 4 months' curing period in brine.

† Two brine samples representing two different ages of fermentation were taken from the vats at Plant F.

** Brine from vats drained off and new brine added prior to test. Undoubtedly part of enzyme was lost.

†† No. 1, up to 1⅛ inches in dia.; No. 2 up to 1½ inches; No. 3 above 1½ inches. Mixed refers to all three sizes.

TABLE 7

*Summary of Enzyme Activity Studies of Commercial Brines*

| Item | Polygalacturonase Activity | |
|---|---|---|
| | Positive | Negative |
| 239 Brines Examined | 74 (31%) | 165 (69%) |
| 9 States Sampled | 6 | 8 |
| 19 Salting Sta. Sampled | 6 | 18 |
| % Loss in Viscosity | 5-54 | 0 |
| Firmness of Cured Stock | Mushy—13 lbs. | 16-22 lbs. |
| Brine Strength | 10-21% | 12-19% |
| Total Acidity as Lactic | 0.2-1.2% | 0.2-0.9% |
| Brine pH | 3.2-3.9 | 3.4-4.0 |

## Conclusions

Two methods for measuring the polygalacturonase activity on pectin solutions were tested: (1) Loss in viscosity of a standard pectin solution, and (2) liberation of aldehydic groups by hydrolysis. The viscosity method was capable of detecting enzyme activity in extremely low concentrations. The enzyme concentration of the cucumber fermentations was too low to liberate aldehydic groups at sufficient rate to be measurable with iodine solution.

A polygalacturonase-like enzyme was found in commercial cucumber fermentations and was considered responsible for softening of salt-stock under commercial conditions. The enzyme found was active in brines from numerous commercial brining stations and was commonly found under conditions of salt concentration, acidity, pH, and temperature which prevailed at plants operating in various parts of the United States.

The polygalacturonase-like enzyme from cucumber fermentations and the commercial polygalacturonase (Pectinol) reacted alike to adjustments of pH, temperature, salt, and time of incubation. The maximum activity of both enzyme systems was at pH 4.0 and 30° C. Increasing the salt concentration up to 21% by weight (80° salometer) did not inactivate polygalacturonase in either the commercial preparation or the active brine.

Firm, cured, cucumber salt-stock from commercial source was softened by the addition of polygalacturonase to the brine.

The relative viscosity of the standard pectin solution was influenced by pectin concentration, pH, temperature and addition of sodium chloride. All of these factors must be controlled to insure accurate measurements, and for making quantitative comparison.

The enzyme pectinesterase was found in certain cucumber fermentations and in such cases produced a gel with pectin in the presence of polyvalent ions.

## Acknowledgments

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We are also indebted to the cooperating pickle plants of the National Pickle Packers Association which provided samples for study.

## Addendum

After this article was written, it was observed that with certain brines, the pectinesterase produced a gel in the presence of polygalacturonase. This reaction obviously blocked the determination for the polygalacturonase by the viscosity test. To eliminate the gelling action of pectinesterase, the brines, containing a few drops of toluene as a preservative, should first be incubated at 40° C. for 24 to 48 hours. The test is then carried out as described in the article.

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# Industrial and Legal Viewpoints

## Technological Problems in the Fishery Industries[a]

H. E. CROWTHER
*The Atlantic Coast Fisheries Company, Boston, Mass.*

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**Technological problems encountered in processing fish are described.**

To the average person, the mention of the fishing industry means a trip on a small sports fishing boat, or buying fish at a neighborhood retail fish store. Very few realize the size and scope of this industry. It isn't as large as the meat industry, of course, but it isn't a small business by any standard. In an average pre-war year 4,400,000,000 pounds of fish were landed, with a final sales value of $596,000,000.

All industries have problems, but the fishing industry has more than its share. The following are a few of the major ones.

The first problem is not strictly a technological one but it has a marked effect on the technologist. The problem is that the fishing industry is a very old established industry which is set in its ways. Most of the people in it have grown up in the industry, and incidentally have made money in it. To them, the methods they have been using for years are satisfactory, and they are reluctant to accept new procedures until their competitors have tried them and have found them an advantage which is expressed in dollars and cents. This is to be expected in an industry having the history and background of the fisheries, but it makes the technologist's work difficult. If he is fortunate enough to work out his problems successfully, he must then sell his superiors, or the industry, on the ideas in order to put them into effect. It is difficult, but it can be done—and has been done—and each success makes the industry in general more receptive to new ideas.

A second problem, along the same lines, is that most of the companies in the fisheries are small and cannot afford research even if they wanted it. This means that with the exception of a few of the larger companies, all of the research for the fisheries must be done by the Government, State or University laboratories, and the support which has been given to Government research has not been great. For example, in a typical pre-war year the Government spent 82c per ton of food in the fisheries and $7.04 per ton of food in agriculture.[b] The industry needs technologists and technological research but how to get them is a problem.

One of the complicating factors in fisheries is that there are over 550 species of fish and shell fish in the United States, and nearly every species of fish is markedly different from the other. Also, even within each species there is often a difference in texture, keeping quality, and flavor, depending on the locality in which the fish are caught. With each species there is a problem for the technologist. Different species of fish can not all be handled the same. There are peculiarities all along the line from the actual method of catching through plant processing, and even into final retail sales. It is a well known fact that the people in certain areas of this country like one type of fish and will have no other, while other sections have opposite tastes. New England, for example, likes haddock over cod in a ratio of approximately 5 to 1. In some mid-west sections cod far outsells haddock. Pittsburgh likes whiting while certain other sections will not touch it. The big question is why all sections do not eat all types of fish. Perhaps it is a matter of education. Whatever the reason, it helps to make fish handling difficult and gives the technologist another headache.

In order to give a better understanding of specific problems which are encountered in handling fish, a brief background of how fishery products are prepared for marketing is given. There are four major methods of preparing fish for shipment to the wholesale or retail market.

The first type is known as "round." This is a fish just as it was taken from the water and includes head, scales and entrails.

Second, are the "dressed and scaled." These fish have had the heads, entrails and scales removed but are not otherwise cut. Of course there are other variations of these methods, but they fall between these two.

Third, are fish steaks. Large fish are used for this and the steaks are made by cutting the cleaned or "dressed and scaled" fish cross-wise, through the backbone, into sections approximately ¾" to 1" thick. Such a steak will be almost circular in shape with skin on the outer surface and the cut backbone in the center.

The fourth method is fish fillets. Fillets are the meaty sides of the fish which are cut away from the backbone. They are lengthwise cuts. They may either be skinned or the skin left on depending on the species. Cod fillets, for example, are always skinned—haddock very seldom. Fillets are by far the most popular means of handling fish for they save on transportation by not having to ship the bones or other inedible parts. They are also the most convenient for the housewife to handle and are practically 100% edible.

Shellfish are handled a little differently. Oysters and clams, for example, are either shipped alive in barrels or are shucked and shipped in water-tight containers. Lobsters and crabs are either shipped alive or they are cooked at the source of supply and the meat picked out and put in containers and shipped in ice.

These, in brief, are the four major methods of preparing fish. For each of these methods there are seven or eight variations in handling.

[a] Given at February 7, 1949 Meeting of the Institute of Food Technologists.

[b] Fishery Resources of the United States, 79th Congress, 1st Session, Senate Document No. 51, March 1945.

First, fish may be shipped or held in crushed ice. The ice, of course, lowers the temperature of the fish and delays spoilage by retarding bacterial multiplication. Round, and dressed and scaled fish are usually packed directly in the crushed ice—the skin acting as a protection against the melting ice. Fillets and steaks however are wrapped in parchment paper or cellophane and packed in slip-top metal cans, which are then packed in ice. The metal of the can conveys the cold to the fillets and keeps the fillets wrapped and clean. The cellophane, in combination with the can, prevents the water from the melting ice from leaching the soluble proteins from the cut surface of the fillets and thus reducing the flavor.

In New England, undoubtedly the most important method of keeping fish is by freezing. In January, 1949, there were 150 million pounds of frozen fish in U. S. freezers. All cuts of fish are frozen—from the round to the fillets. The whole type fish, with the skin on for protection, are either frozen loose in stacks or are put in large pans and frozen in blocks. The fish are held together in the block when the water between the closely packed fish freezes. Fillets and steaks which are to be frozen are first wrapped in cellophane or other suitable wrapping material and then packed in 5 or 10 pound waxed cardboard cartons and then placed in the freezer. The trend now is to pack the frozen 5 and 10 pound cartons of fish in 50 pound corrugated master cartons for ease in handling and shipping. The average temperature used for freezing the fish is from 20 to 30 degrees below 0° F. The temperature for frozen storage is approximately 0° F.

Another method of keeping fish is by smoking. The smoking of fish serves two purposes—first, to give the fish a distinct flavor, and second, to prolong the storage period before objectional changes or deterioration occurs. There are a number of degrees of smoking, ranging from a very faint smoked color, odor, and flavor to heavy, hard smoking as in kippers and dry, smoked fillets. In general, the heavier the smoke the longer the fish remain edible. Smoking is usually accompanied by some degree of salting. Light smoked and light salted products require refrigeration to prevent spoilage. This applies to such products as Finnan Haddie. The heavy smoked, heavy salted products will not spoil even if stored at room temperature.

Still another method of preserving fish is to salt them. The whole or split fish are packed with layers of salt in such a way that the fish make their own brine. Excess of salt is added so that any excess water from the fish will be taken up.

In combination with the salting is the process of drying the fish. Usually the fish are first heavily salted and held in the salt until the salt "strikes" or penetrates the entire depth of the fish. Then the fish are either dried in the air or by mechanical equipment until the moisture content is under 50%. Fish with a moisture content of 40% or lower will last almost indefinitely at room temperature.

Another method of keeping fish is to pickle them in a combination of salt, vinegar and spices.

The last, and perhaps the most important method of preserving fish is by canning. The problems experienced in canning fish are not too different from those in the normal food canning industry.

Approximately one-fourth of the fish caught do not find their way into the food markets. These fish are used to manufacture by-products. For the most part, that means that they are converted into fish meal and oil.

In each method of handling fish there are many problems, as there are with any food product, but in the fisheries the biggest of all is spoilage. To the average person there are only two classifications of the quality of fish. It is either fresh and edible, or spoiled and inedible, the spoilage being determined by the odor. The fisheries technologist knows that from the day the fish are caught, they begin to lose their flavor and that the loss in flavor is inversely proportional to the care with which they are handled. It is possible for fish to have no objectionable odor, and still be practically devoid of flavor. Unlike meat, the flavor of fish does not improve with age, so there is nothing in fresh and frozen fish processing which allows for the aging of the product.

With each of the previously described methods of handling or keeping fish, spoilage problems are encountered. The following are examples of the problems which may be present in each of the methods.

The first is fresh fish, and by "fresh" is meant "not frozen." Fish are classified by the trade as "fresh," "frozen," and "canned," depending upon the method of preservation. In the round uncut fish, as it is caught, the process of spoilage which occurs, is somewhat different from that of fillets. The skin acts as some protection against outside bacterial contamination, so spoilage naturally occurs from within. As soon as a fish dies and goes through rigor mortis—the enzymes of the flesh begin to act on the protein, and soften it. At the same time, the bacteria within the entrails begin to multiply and finally break through the entrail cavity wall and come in contact with the flesh. Since the enzymes have already prepared the flesh, the bacteria find a good medium for growth. In fish this action is very fast and therefore one of the essentials in processing fish is speed. It is a continual race with fresh fish to get them landed, to the plant, in ice, and to the retail market in the shortest possible time. With fish to be frozen, it is a race against time to get them in the freezer.

Fillets and steaks are very similar in regard to spoilage since both have cut surfaces of the flesh exposed. The fillets, for example, are cut from fish on specially designed tables in the plants. In many plants whole fish are handled on the same surface on which the fillets are cut. On this surface the whole fish deposit a slime material which is very viscous and difficult to remove by water. The slime is also a medium for bacteria growth. Also, bacteria laden material from the entrails may further contaminate the table surface. Therefore, when the fillet is cut, and the cut surface comes in contact with the contaminated table, it picks up large numbers of bacteria which may start the fillet on its way to spoilage. Since the flesh naturally is relatively soft, delicate and watery, it is not difficult for the bacteria to penetrate between the segments of flesh. Contamination of the fillet surface also comes from the knives and hands during handling.

With frozen fish, the spoilage problem is somewhat different than with the fresh. Of course, in the time elapsing between catching the fish and freezing it, all of the spoilage problems associated with fresh fish are present. The quality of frozen fish is directly dependent on the condition of the fish as it is frozen. Freezing will arrest spoilage, but it will not improve the quality of the flesh. In the fish industry, one of the most difficult points for the technologists to get over to production management, is that fish is no better after it is frozen than it was before it reached the temperature of zero. The tendency is for inexperienced men to consider freezing as a place to put questionable fish, since the time between processing and freezing will be much shorter than the time between processing and fresh retail sales.

With "round" fish which has been properly frozen, the main problem is "dehydration." To overcome this, the normal procedure is to glaze the fish by dipping the frozen fish in water and allowing a complete thin film of ice to form around the entire fish. A glaze must be replaced every few months because of evaporation.

With fillets and steaks, glazing is not practicable, and since there is no skin on one surface to act as protection, the fillets must be wrapped in a moisture vapor resistant material, such as cellophane. If the fish are not wrapped so as to cover the entire fillet, or if an inferior grade of wrapping material is used, the effect of dehydration will appear on the surface during frozen storage.

With oily fillets, there is an additional problem of rancidity or oxidation of the oil on the surface of the flesh. The use of proper wrapping technique, and the proper wrapping material will go a long way toward retarding oxidation of the oil.

It has been learned through experience that one of the biggest problems in handling frozen fish, especially fillets, is the fluctuation in temperature to points above 0° F. during storage. This will not only lower the quality of the fillets in regard to flavor and texture, but will help to increase what is known as "drip" in thawing. "Drip," of course, is the release of the water soluble components from the protein.

In general, the lower the temperature during freezing and during frozen storage, the better the quality. However, there is a point below 0° F. where it becomes uneconomical to hold fish in frozen storage because of the cost of maintaining the low temperature.

Time does not permit a discussion on the problems of fish smoking, salting, drying and pickling operations, but I can assure you that each of these operations is an industry within itself, and each has problems peculiar to that industry.

In the canning industry, which is perhaps the largest phase of the fishing industry, there are all the problems encountered by anyone in the food canning business, and then some. Handling different species of fish is almost the same as handling different varieties of vegetables, for the canning procedure for each must be worked out to suit that particular species. Some fish products must be brined or otherwise treated before canning, or they will disintegrate following retorting. Exhaust box time and processing time must be adjusted for each. Even within the species themselves, fish from different localities require adjustments in canning technique. For example, a California company recently encountered a problem of canning pilchard fillets on the West Coast. They had been packing fillets in Monterey, California, for years without trouble. However, when they tried to can fillets from fish that were caught 150 miles south of Monterey, the product was completely different. The buyers noticed the difference in flavor, texture and appearance immediately, so it was necessary to determine the cause of the trouble and adjust the canning operation to take care of it.

In the fishing industry there are new problems of this type every day and, because of the variety of problems encountered, technologists should never have cause to say that their job is monotonous; also it is not likely that within the next 20 years a good technologist in the fishing industry will have an opportunity to say that his job is finished and he has nothing else to do.

## INSECTS COMMONLY FOUND IN MEAT PACKING PLANTS

Article by Richard Rich (Entomologist, West Disinfecting Company) published in *Modern Sanitation* 1, 28 (July, 1949).

One of the greatest conflicts is that between man and insects—neither side has won the war and the battle goes on. Almost every meat packer can readily state a figure which represents the cost of insect infestation in his plant. It is comparatively simple to itemize the number of labels damaged in his plant, the amount of products contaminated, and storage losses due to insect infestations. However, the meat packer too often ignores the more intangible losses he is suffering due to decreased production, loss of morale, absenteeism, and the general nuisance of insects within his plant.

Of all the many insects in the United States, the meat plant operator will find the 18 species listed to be of most common concern.

The insect pest must not be combatted only during its adult stage. Hiding and breeding places of the insect must be found and treated with insecticides which can penetrate into the cracks and crevices to which the insect is generally drawn. Apparently the most practical and effective method of destroying the pest—in its formative and adult stages—is to diffuse liquid insecticide in a dense fog throughout the entire meat plant at the same time.

The author lists the following species and gives their size, color, fecundity, life cycle, characteristics and habitat:

1. German Roach
2. American Roach
3. Oriental Roach
4. Cheese Mite
5. Confused Flour Beetle
6. Crab Louse
7. Indian Meal Moth
8. Larder Beetle
9. Pharaoh Ant
10. Drain Fly
11. Fruit Fly
12. Hide Beetle
13. House Centipede
14. House Cricket
15. House Fly
16. Pill Bug
17. Red-legged Ham Beetle
18. Silver Fish

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# Easter Reveries

Are technologists human? Yes, they are real people —like you and me, each endowed with his own individual ambitions, ideals and ethics—yes, and with his full share of human frailties.

The buzzard in God's clear sky seeks out the carrion on the Earth far below him. He sees only the bad amidst so much good. Some men are like that. It's so easy to find fault, to see the misdeeds of others, to listen to stray gossip about a fellow man—and, for good measure, to throw on the hot embers of rumor a few red-hot coals of hearsay!

Do you criticize unjustly your fellow workers, your employer, your competitor — your Institute? Is the criticism truthful and constructive, or is it based on rumor or on what you would like to believe? We Americans are proud of our right to speak and write as we believe. A man can choose his own friends, but he cannot always choose his business associates. A kind word or deed begets another in return. Remember the old platitude, "There's so much good in the worst of us, and so much bad in the best of us . . . "? Let us look for the good, the true, and the noble in men. Unkind thoughts are better left unspoken. The world is too full of friendliness, chivalry and kindness to probe for the evil and the muck in a man. The Golden Rule can be applied to everyday life, "Do unto others as you would have others do unto you." Hold that biting tongue—think, before you speak. Drown that rumor! Give that gossip the silent treatment!

After all, Bill and Hank and even old Moneybags, who lives in the big house on the hill, aren't such bad fellows—*if* you look for the *good* in them.

CARL R. FELLERS
President, I. F. T., 1949-1950

## RETENTION OF IRON IN HUMAN BLOOD

Once it reaches its destination, iron remains in the body system to be used and reused for more than six months after it is taken in, according to recent findings in the department of food technology at the Massachusetts Institute of Technology.

"This is particularly remarkable," says Dr. Robert S. Harris, professor of nutritional biochemistry, "since other tests have shown that the red corpuscles in the blood, containing most of the iron in the body, are destroyed and remade on the average of once every 23 days."

Thus the M. I. T. studies indicate that iron is not a permanent but a transient component of human blood, able to move through several cycles of the destruction and creation of haemoglobin, the compound which gives blood its red color.

The fact that iron does remain in the body of a normal adult for such a long period, Dr. Harris points out, may mean that the required daily intake of iron is somewhat less than the published figures now indicate. The currently-accepted daily minimum requirement of iron is 12 milligrams (about .0004 ounce), according to National Research Council standards. Both in the blood and in tissues, iron compounds perform many vital functions in the body.

Studies leading to these results, made by the use of small amounts of radioactive iron, were designed to determine the effect of certain food substances on the assimilation of iron.

All cereals contain compounds known as phytates, which are thought to interfere with the utilization of minerals in the diet. Dr. Harris' conclusion from his studies is that unrefined cereals containing phytates interfere with iron assimilation no more than foods which contain no phytates. Oatmeal, for instance, had no effect.

On the other hand, phytates in soluble form markedly impeded iron absorption when they were added separately to a meal. Apparently, says Dr. Harris, cereal phytates are bound up so that they cannot react with the iron.

With the permission of their parents, 17 adolescent boys participated in the M. I. T. experiments over a period of more than one year, eating different types of breakfasts each of which included a small amount (8 milligrams) of iron. A minute fraction of this iron was a radioactive isotope, which could be easily traced in its course through the body. These "tagged" atoms were used to determine the amount of iron which appeared in the blood stream from each breakfast.

In general, Dr. Harris' results indicate that about 10 days were required for all the iron absorbed from a single meal to reach an equilibrium quantity in the blood stream. After that, no measurable loss of this iron was found during a test period of 175 days.

Only one-fifth as much iron was absorbed when taken with a full meal as when taken alone with a glass of water—a fact which suggests, according to Dr. Harris, that medicinal iron would be much more effective if taken between meals than at mealtimes.

Similar studies of the absorption of calcium by the body are now underway in M. I. T. food technology laboratories, using a radioactive isotope of this vital bone-building substance.

## MONOSODIUM GLUTAMATE

A memorandum was issued March 28 by the Meat Inspection Division of the Bureau of Animal Industry, United States Department of Agriculture, outlining the use of monosodium glutamate in sausage, luncheon meat, meat loaf, and similar products.

Pure monosodium glutamate is already used by processors to enhance the flavor of many foods, notably soups, baby foods, canned and fresh dressed poultry and bouillon cubes.

Thus, the privilege of including it in meat food products now offers processors a proven avenue of intensifying the natural flavors of these products also.